

**EFFECTS OF ACID MINE DRAINAGE ON THE RELEASE OF ALUMINUM FROM
CLAY MINERALS**

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The objective of this PhD research was to investigate the leaching of acid clays with acid mine/rock drainages (AMD/ARD) typically found in U.S. soils and develop information supporting the phenomena of the release of elevated concentrations of aluminum from such interactions. In Pennsylvania, reported aluminum concentrations in discharge samples from 140 abandoned coal mines showed that over 50% of these water samples presented dissolved aluminum concentrations over 1 mg/L. Aluminum at these levels can be detrimental to freshwater aquatic ecosystems and thus, these data suggest that aluminum-containing AMD/ARD is a major problem in USA.

Leaching of smectite clays with different synthetic AMD/ARD were conducted to explore the effect of common cations in pyritic and brackish/saline AMD/ARD, on the release of aluminum from clays at pH between 2 and 3 frequently found in the field. The major finding of this research is that the release of aluminum from smectite clays is enhanced by Fe^{2+} , potassium (KCl) and sodium (NaCl) salts in AMD/ARD. The major mechanisms involved in the release of aluminum from these clays were: cation-exchange dominating the short-term and clay dissolution dominating the long-term leaching of aluminum from smectites. These results were consistent with the low iron concentrations and high aluminum concentrations observed in some field AMD/ARD.

The outcome of this research adds new knowledge to the field of environmental science and engineering by pointing out the significant effects that K and Na salts in AMD/ARD have on the release of aluminum from clays. These K and Na salts in AMD/ARD promote the release of Al from field clays leading to deleterious effects on aquatic ecosystems. Thus, this research contributes to a better understanding of the occurrence of elevated levels of aluminum in AMD/ARD and will assist others to consider alternative remediation strategies in those locations where the *in situ* generation of high concentration of aluminum discharges may occur. The observation of greater concentrations of aluminum in leachate produced by brackish AMD/ARD implies that highway deicing salts in road runoff could aggravate the leaching of aluminum from pyritic rocks used as fill or exposed in road cuts.

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1.0 INTRODUCTION

Acid Rock Drainage (ARD) occurs naturally, as part of the rock weathering process, in environments with the presence of sulfide minerals such as pyrite. ARD, however, can be worsened because of anthropocentric activities such as mining and construction. Acid rock drainage associated with mining operations is commonly termed acid mine drainage (AMD). The primary contaminants in AMD/ARD generated in a pyritic environment are iron and sulfate. In the presence of aluminum-bearing underground geology, the *in situ* generation of aluminum discharges is favored. For instance, the mining of rich metal sulfide and sulfosalt deposits near argillic zones is associated with high potentials for the generation of AMD. These acidic discharges may contain thousands of mg/L of iron and aluminum, as well as other metals of concern (du Bray, 1996).

Aluminum (Al), is an important contaminant because of its potential for deleterious impacts on the environment. The U.S. Environmental Protection Agency (1992) secondary maximum contaminant level (SMCL) for aluminum in drinking water is 0.05 to 0.2 mg/L, based on aesthetic effects. Although safe from a point of view of drinking water quality, aluminum at these levels can be detrimental to freshwater aquatic ecosystems (Baker and Schofield, 1982). The U.S. Environmental Protection Agency (2009) criteria continuous concentration (CCC) and criteria maximum concentration (CMC) values for aluminum are 0.087 and 0.75 mg/L, respectively.

Aluminum contamination of natural surface waters and aquifers due to AMD/ARD is a significant problem worldwide (Gray, 1998). Examples of aluminum-containing AMD discharging in ecosystems are acid waters from a mine site at Sobov, Slovakia, with 1,100 mg/L (Dubiková et al., 2002), and AMD with aluminum concentrations over 50 mg/L from an affected location at Huelva, Spain (Galan et al., 1999). In United States, data collected from over 150 different mine drainage sites showed dissolved aluminum concentrations in AMD in excess of 800 mg/L (Watzlaf et al., 2004). Over 30% of these locations presented minimum dissolved aluminum concentrations of 50 mg/L. These data show that aluminum-containing AMD/ARD is a widespread problem in USA.

Aluminum levels in AMD/ARD are increased at low pH values, as showed by Cravotta (2008a, b) who reported median aluminum concentrations in mine discharge samples from 140 abandoned coal mines collected in summer and fall 1999 in Pennsylvania. Over 50% of the 140 abandoned mine discharges sampled presented median dissolved aluminum concentrations over 1 mg/L. The highest median concentrations of aluminum were found in the acidic range of pH 2-5 with values between 1-108 mg/L of aluminum.

Elevated aluminum levels in AMD often occur when the underground geology is characterized by the presence of aluminum bearing minerals. Typical of such soils include clays containing the mineral kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Smoke, 2007; Sidenko et al., 2005) and smectite, $\text{M}_{0.33}[\text{Mg}_{0.66}\text{Al}_{3.34}][\text{Si}_8]\text{O}_{20}(\text{OH})_4 (\text{H}_2\text{O})_n$ -where $\text{M}_{0.33}$ commonly represents 0.33 exchangeable divalent cations (generally Ca) or 0.66 monovalent cations (generally Na or K) (Metz et al., 2005; Astudillo, 2004)-. Kaolinite, has been reported as one of the most valuable mineral sources of wealth in Pennsylvania (Brown et al., 1913). Fire clays, which are clays essentially from the kaolinite group, are also known to occur in enormous quantities associated

with coal beds (Shaw, 1928). Galan et al. (1999) and Sidenko et al. (2005) have shown that kaolinite is a possible reaction product of the dissolution of unstable smectite under acidic conditions. Smectites are the most common phyllosilicates in soils and sediments (Sondi et al., 2008) and are broadly found in the northern hemisphere, including U.S. soils (Astudillo, 2004). The prevalence of smectite and other aluminum bearing minerals in soils in the Appalachian mining region of the U.S. increases the potential for the generation of ARD with high concentrations of aluminum.

EPA estimates that over 95% of the acid problem in U.S. is located in the Appalachian region including western Pennsylvania, almost all West Virginia, southwestern Virginia and far western Maryland. Other U.S. regions such as the Western region, including Wyoming and the Interior region, including Texas, historically support high mining activity and AMD problems as well. Thus, these regions have elevated potentials for the generation of AMD with high concentrations of aluminum due to the abundance of kaolinite, smectite, as long as other aluminum-bearing minerals.

1.1 PROJECT BACKGROUND

In Pennsylvania, acid mine/rock drainages have been historically associated with the mining industry, but can also be attributed to earth moving projects such as highway or dam construction (Smoke, 2007). One example of ARD contamination is from a Centre County site in Pennsylvania. The contamination has been traced to the construction of a highway embankment along I-80 and directly over the Jonathan Run stream (Smoke, 2007). The stream flows through a

concrete culvert under this embankment and aluminum precipitates are seen at the exit and downstream of this concrete culvert.

The embankment was constructed using locally available fill material. Exploratory drilling through the embankment revealed the presence of sandstone boulders and pyritic and clay material in the fill and confirmed it as the main source of aluminum-containing ARD discharging into the Jonathan Run stream (Smoke, 2007). There are no mineralogical analyses or characterization of the fill clay material at this site. Groundwater samples collected from the boreholes throughout the embankment showed the presence of groundwater aluminum and iron concentrations as high as 160 mg/L and 173 mg/L, respectively, near the culvert (Hedin Environmental, 2003; GAI Consultants, 2007; Neufeld et al., 2007). However, the surface seepage from the embankment and discharging into the Jonathan Run stream consistently had low concentrations of iron (<2 mg/L) concomitant with elevated concentrations of aluminum (≈ 48 mg/L). It therefore follows that iron is being retained within the subsurface sandstone-clay soil embankment.

1.2 SCOPE OF RESEARCH

Kaolinites and smectites are extensive families of aluminum-bearing clays in U.S. soils, often associated with the presence of sulfide minerals, such as pyrite, and the mining activity. Field aluminum-bearing soils associated with AMD/ARD impacted areas are frequently mixtures of these families of clays, along with other weathered minerals. Leaching of these field soils with AMD/ARD often results in AMD/ARD with significant concentrations of aluminum in the acidic pH range <4.

The release of aluminum from most families of clays, including kaolinites and smectites, has been broadly studied under particular conditions. These conditions include studies of proton-promoted dissolution of clays, including pH ranges from 2 to 3, and exchange reactions involving clays in saline environments. Although these studies explore the mechanisms and factors involved in the release of aluminum from these clays while exposed to acidic and saline environments, respectively, their findings can not fully apply to different leaching solutions such as acid mine/rock drainages. Thus, the phenomena leading to generation of elevated levels of aluminum in AMD/ARD is not completely understood. The pH is known to be a chief factor on the release of aluminum from clays. Nevertheless the effect of metal cations in AMD/ARD on the release of aluminum from these clays has not been totally addressed. Hence, fundamental information supporting the phenomena of generation of elevated levels of aluminum in AMD/ARD still needs to be developed.

The overall goal of this study was to better understand the factors and mechanisms involved in the generation of high concentrations of aluminum in AMD/ARD. The study investigated and explained how subsurface pyritic discharges influence aluminum release from clay minerals under conditions typically found in mining regions. Based on preliminary research, my investigation focused on the effects of underground AMD/ARD with brackish/saline salts on the release of aluminum from clay minerals. In particular, the influence of ferrous ions, Fe^{2+} , sodium ions, Na^+ , and potassium ions, K^+ , in AMD/ARD on the release of aluminum from widespread smectite clays was studied.

In order to accomplish the overall goal, several specific experimental objectives were developed as listed below:

1. The evolution of the aluminum released from smectite clays when leached with synthetic sulfuric acid solutions starting at pH values in the range of 2 to 3; a range that leads to the incidence of significant aluminum released from clay minerals, was evaluated.
2. The evaluations above were refined by incorporating Fe^{2+} , Na^+ and K^+ at concentrations that are found typical of non brackish and brackish/saline acid rock/acid mine drainages.

The outcome of this PhD research helps to understand and quantify factors leading to aluminum generation and discharge from acid mine and acid rock drainages. This knowledge will assist in a better understanding of the occurrence of high concentrations of aluminum in AMD/ARD by pointing out the significance of high concentrations of Fe^{2+} , Na^+ and K^+ in AMD/ARD on the release of aluminum from widespread smectite clays.

2.0 LITERATURE REVIEW

2.1 CLAY MINERALS

The Association International pour l'Etude des Argiles (AIPEA) and the International Mineralogical Association (IMA) Committee on New Mineral and Mineral Names has adopted an hierarchical approach to the classification of clays based on types, groups, subgroups and species of phyllosilicates (Essington, 2004). Some of the most interesting clay species and their generalized formulas from the point of view of this research are summarized in Table 1 from the approximately thirty different types of clays in these categories.

Clays are classified based on the type of layer (1:1 or 2:1) at the division level; where the first digit refers to the number of tetrahedral sheets and the second digit refers to the number of octahedral sheets in the layer. It follows a group classification according to layer charge, where kaolinite, illite and chlorite groups are exceptions. For kaolinite minerals, the distinguishing characteristic is the octahedral occupation (used at the subgroup level). Within each group, clays are further sub-grouped based on the octahedral site occupancy usually found in nature: trioctahedral; when all octahedral sites are filled; and dioctahedral when 2/3 sites are filled (Giese et al., 2002). The illite which is dioctahedral by definition is excluded.

The ideal structures of kaolinite and montmorillonite (dioctahedral smectite), the most interesting species of clay minerals from the point of view of this research, are shown in Figures 1-2 to illustrate the typical arrangement of layers. Most clay materials in nature are mixtures of these different types, along with other weathered minerals. In kaolinite, each layer is composed of 2 different sheets; ideally, one Si-O tetrahedral sheet with Si in the centre of each tetrahedron and one octahedral sheet with Al in the centre of each octahedron. The layer of kaolinite presents dioctahedral occupancy. This is to say 2/3 parts of the octahedral sites are filled. In the kaolinite layer: i) each octahedral sheet forms one basal plane where $>Al_2OH$ (aluminum-hydroxyl groups) can be found; ii) and each tetrahedral sheet forms a different basal plane known as silanol/siloxane basal plane (Figure 1).

In montmorillonite each layer is composed of 3 sheets: two tetrahedral sheets surrounding one octahedral sheet, as shown in Figure 2. In contrast to kaolinite, the layer of montmorillonite presents significant isomorphic substitution. Isomorphic substitution is the replacement of atoms in the crystal structure for other atoms without affecting the crystal structure. For montmorillonite, it can take place in both the silica tetrahedral and the aluminum octahedral sheets. Thus: i) in addition to Al, Fe, and Mg may occupy the centre of each octahedron ii) and in addition to Si, Al may occupy the centre of each tetrahedron. These substitutions will have consequences on the surface charge (will lead to an excess of negative surface charge) of clay particles as well other clay properties, such as the cation exchange capacity (CEC).

Table 1. Formulations of some common clay minerals

¹ Division (Layer Type)	Group (x= Layer charge per ½ Unit cell)	Subgroup (Octahedral Occupation)	Species	Ideal structural formula
1:1	Kaolinite	Kaolinites (dioctahedral)	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
2:1	Smectite ($0.2 < x < 0.6$)	Dioctahedral Smectites	Montmorillonite	$\text{Na}_{0.4}(\text{Al}_{1.6}\text{Mg}_{0.4})\text{Si}_4\text{O}_{10}(\text{OH})_2$
	Illite ($0.6 < x < 0.9$)	Illites (dioctahedral and non-expansive)	Illite	$\text{K}_{0.8}(\text{Al}_{1.8}\text{Mg}_{0.2})(\text{Si}_{3.4}\text{Al}_{0.6})\text{O}_{10}(\text{OH})_2$
	Mica (x~1)	Trioctahedral micas	Biotite	$\text{K}(\text{Fe}^{\text{II}}_{1.5}\text{Mg}_{1.5})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$
	Chlorite x is variable	Dioctahedral chlorites	Donbassite	$\text{Al}_{2.27}(\text{OH})_6\text{Al}_2(\text{Si}_{3.2}\text{Al}_{0.8})\text{O}_{10}(\text{OH})_2$

¹Essington (2004)

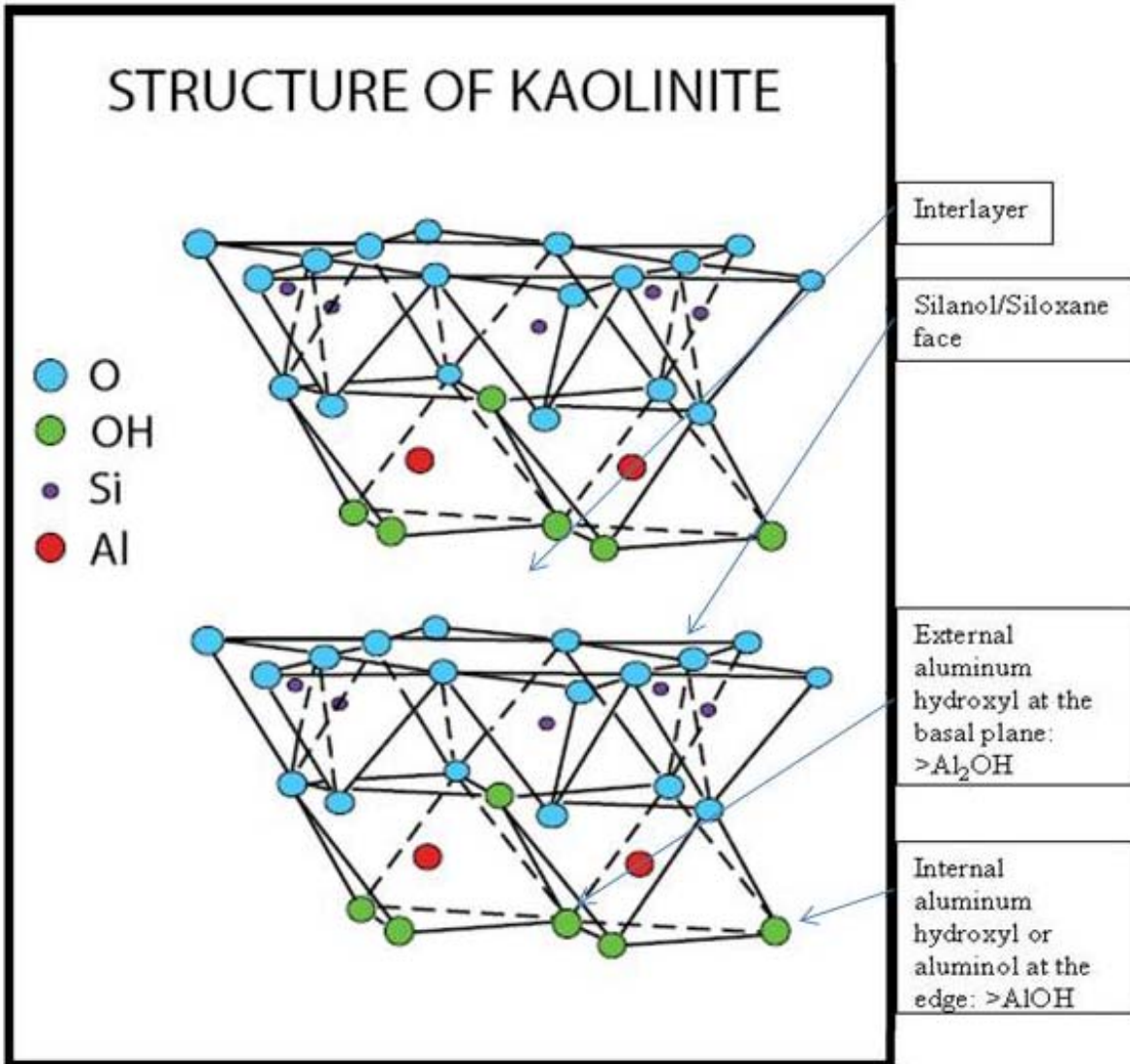


Figure 1. Ideal structure of kaolinite

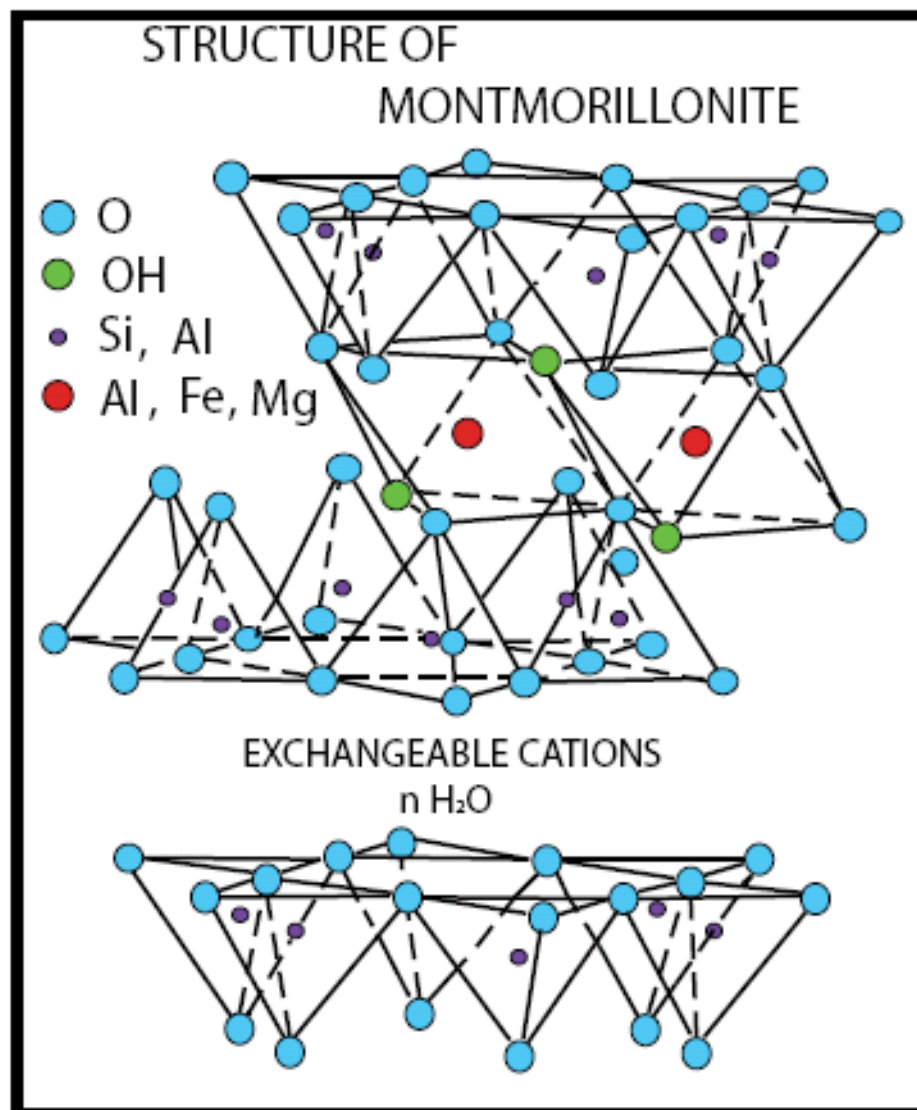
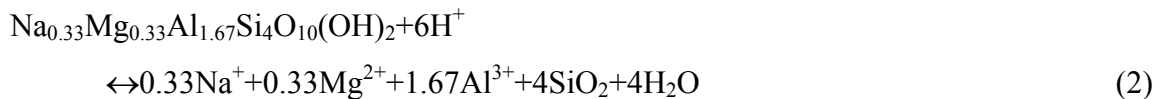


Figure 2. Ideal structure of montmorillonite

2.2 ALUMINUM RELEASE FROM SOILS

The release of aluminum from the constituents of soils may be due to exchange from cation-exchange sites, the dissolution from amorphous mineral phases, or the decomposition/mineralization of organic forms (Driscoll and Postek, 1996). The oxidation of pyrite and consequent development of low pH (<4) typically generates elevated Fe^{2+} and H^+ levels in AMD/ARD, above background concentrations, and may result in the release of aluminum from clay minerals by ion-exchange (Tan, 2000) and dissolution processes (Essington, 2004). The presence of anions such as SO_4^{2-} in AMD/ARD may also increase the concentration of aluminum, due to aqueous complexation reactions (Cravotta, 2008b; Pu et al., 2010). In the presence of smectite clays, such as sodium-saturated montmorillonite, $\text{Na}_{0.33}\text{Mg}_{0.33}\text{Al}_{1.67}\text{Si}_4\text{O}_{10}(\text{OH})_2$, these processes can be illustrated as follows:



Where, Al-Mont. and Me-Mont. represent an exchangeable aluminum (Al) and metal (Me^{n+}) ion in the smectite (montmorillonite) adsorption complex, respectively.

2.3 DISOLUTION REACTIONS IN CLAYS

Common soil minerals, such as silicates, have strong chemical bonds between their cationic constituents, M^+ and oxygen. These bonds which will be represented: $>M-O$, hold the constituents in the mineral structure. To dislodge this framework of ions it is necessary to create a strong perturbation of these bonds. Highly polarizing species such as the proton, H^+ , or a ligand that forms inner-sphere complexes, may release these cations from the mineral structure. In AMD/ARD environments hydrogen ions, H^+ , are dominant and control the dissolution of secondary minerals, such as clays.

The dissolution reaction rates of clays are generally slow in contrast to the exchange reactions rates which are typically fast (Li et al., 2006). The proton-promoted dissolution of a variety of clays has been widely studied (Shaw et al., 2009; Rozalen et al., 2009; Gates et al., 2002; Komadel et al., 1996). The proton-promoted dissolution of clays, such as kaolinite, can be illustrated as follows: proton attack begins with H^+ adsorption by the anionic constituents of the clay, e.g: OH^- of the $>Al-O$ bonds. There are 2 evident types of surface hydroxyl (OH^-) groups in the kaolinite structure: $>Al_2OH$ at the basal plane and $>AlOH$ at the edges ($>Al_nOH$ surface groups, where $>Al$ represents an aluminum ion bound to the crystal structure). Each of these hydroxyl groups differ in their reactivity with protons. In fact, the pH dependent charge associated with each surface functional group is a function of the number of structural metal atoms bound to the surface hydroxyl and the valence and coordination of the structural metal atoms. The relatively rapid H^+ adsorption results in the formation of the surface complexes $>Al_2OH_2^+$ and $>AlOH_2^+$. It follows the slower polarization process of the $>Al-O$ bond near the

site of proton adsorption, with subsequent detachment of the metal anion complex (Sposito et al., 2008). It has been suggested that the rate of dissolution is limited by the breaking of >Al-O bonds through the formation of these complexes (Huertas, 1999). The contribution of the basal plane to the overall dissolution rate is critical. It provides sufficient structural hydroxyls to be protonated and form surface complexes (Huertas et al., 1999).

Modern studies of dissolution of phyllosilicates involve the use of atomic force microscopy (AFM). This methodology, in contrast to traditional batch experiments, allows in-situ observation of the most reactive surface sites of clay particles at the molecular scale. In general, it has been reported that dissolution is much faster on edge surfaces than on basal planes (Sondi et al., 2008). On the other hand, it has been shown that the higher cation exchange capacity (CEC) and specific surface area of smectite relative to kaolinite clays (Shaw et al., 2009; Meunier, 2005) result in an increased adsorption of H^+ on exchange sites and interaction over a larger surface area. Thus, smectite clays are more susceptible than kaolinite to dissolution with decreasing pH (Gates et al., 2002; Komadel et al., 1996).

Shaw et al. (2009) studied the mineralogical alteration of smectite-rich and other clays after leaching with H_2SO_4 solutions at wt/wt clay to solution ratios of 1:20 and pH values between 5 and less than 0. This study reported that the crystallinity of smectite-rich clays was more vulnerable than the crystallinity of kaolinite clays when these clays were exposed to H_2SO_4 between pH of 5 and below 0. Based on their results, Shaw et al. (2009) presented a conceptual model of the impact of H_2SO_4 on these clays where cations are mobilized from the aluminosilicate inter-layer by substitution reactions with H^+ ions from the H_2SO_4 solution. As the pH decreases to between 3 and 1 the Al-octahedral and Si-tetrahedral layers undergo dissolution. In addition to pH, other factors such as the weathering history and mechanical wear of the source

clay particles, which governs the ratio between basal siloxane and edge surfaces, have been suggested to influence the dissolution rates, and thus the levels of release of Al and Si overtime, of clay structures (Sondi et al., 2008).

2.4 ION EXCHANGE REACTIONS

2.4.1 The surface charge of the solid phase of clays

The surface of clay particles may develop an electrical charge as a consequence of the broken bonds existent in the region of the crystal edges, the substitution within the lattice, and the hydrogen of exposed surface hydroxyls groups that may be exchanged (Ma et al., 1999). Four different types of surface charge contribute to the net total particle charge, σ_p , in soils. Each one of these components can be positive, zero or negative, depending on soil chemical conditions.

The first component termed as structure (or permanent) charge, σ_0 , arises from isomorphic substitutions in clay minerals. Isomorphic substitution is the replacement of atoms in the crystal structure for other atoms without affecting the crystal structure. It can take place in both the silica tetrahedrons and the aluminum octahedrons of the clay mineral (Tan, 2000). The second component charge results from the balance between the moles of protons and the moles of hydroxyl ions complexed by surface functional groups per unit of mass of charged particle. This component is termed the net proton charge, σ_H . It receives contributions from all acidic surface functional groups in the clay, including the edges. So, in addition to the constant substitution charge, σ_0 , clay minerals possess a pH dependent charge along the edges (Bolt, 1976), σ_H . The sum of structural and net adsorbed proton charge defines the intrinsic charge, σ_{in} ,

which represents components of surface charge that develop solely from the adsorbent structure. Consequently:

$$\sigma_{in} = \sigma_0 + \sigma_H \quad (3)$$

The last two types of surface charge account for the charge associated with inner sphere complexes (IS), σ_{IS} , and outer sphere complexes (OS), σ_{OS} . These two types of complexes account for 2 of the 3 possible mechanisms by which ions can adsorb on clay particle surfaces, i.e.: inner sphere complexation, outer sphere complexation (solvated ions) and diffuse-ion swarm (solvated ions). Inner sphere complexation is considered as the molecular basis for the term specific adsorption because the involved covalent bond depends significantly on the particular electron configurations of both the surface group and the complexed ion. On the other side, diffuse ion screening and outer sphere surface complexation, which basically involve ionic bonds, are the molecular basis for the term non-specific adsorption. Non-specific refers to the weak dependence on the detailed electron configurations of the surface functional groups and adsorbed ion that is to be expected for the interactions of solvated species. Thus, the net total particle charge,

$$\sigma_p = \sigma_{in} + \sigma_{IS} + \sigma_{OS} = \sigma_{in} + \sigma_S \quad (4)$$

Where σ_S denotes the Stern layer charge, which represents all adsorbed ions that are immobilized into surface complexes and that do not engage in translational motions that may be linked to the diffusive motions in the diffuse-ion swarm.

2.4.2 Cation exchange capacity of clays

The net total particle charge is finally balanced with certain excess of ions from the surroundings of the clay particle (Sparks, 1999). These ions are adsorbed via diffuse-ion swarm and thus fully dissociated from the surface functional groups and accordingly free to hover nearby in the soil solution. These ions can not be separated from the surface (i.e: taken out of the system) but may be however exchanged against other ions in the solution. During this process of exchange, electroneutrality of the system is maintained without affecting mineral structure (Bolt, 1976). The adsorptive property by which clays maintain cations in this exchangeable status is known as cation exchange capacity (CEC) (Ma et al., 1999). Under favorable conditions, which refer to the accessibility of the exchanger surface to the solution, the rate is very high (half time reaction is a matter of minutes or even less). Aluminum released from aluminum-bearing minerals due to exchange reactions has been reported by Kombo et al. (2003), who studied the interactions of acidic red soil and seawater and observed high concentrations of aluminum (over 50 mg/L) and decrease of cation concentrations in seawater at low pH values (at around 4).

The CEC or quantity of cations readily available for exchange is influenced by many factors. Such factors include: nature of the exchangeable cations, particle size (grinding can change the CEC), temperature, and phase conditions (dilute or concentrated aqueous solutions, organic solvents, solid-state interactions). Since the contribution of σ_H to the net total particle charge σ_p is pH dependent, it follows that the net CEC is also pH dependent. For this reason CEC of clay minerals, as milliequivalents (meq)/100 g, is traditionally reported at a given pH (Bergaya et al., 2006). Usually the CEC is determined at neutrality (pH=7). The CEC determined taking into account the chemical environment of the soil is commonly termed effective cation

exchange capacity (ECEC). Determination of either CEC or ECEC requires the complete replacement of all exchangeable cations by index cations that are not present in the clay mineral sample. The CEC of clay minerals and acid clays commonly found in most AMD/ARD impacted areas, are shown in Table 2.

Table 2. Cation exchange capacities (CEC) of some common clays

Species	$\frac{1}{2}$ - Unit formula	CEC (meq/100 g)
¹ Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	3-15
² H ⁺ -Kaolinite	$(\text{Si}_4)^{\text{IV}}(\text{Al}_{3.89}\text{Fe}_{0.08}\text{Mg}_{0.03})^{\text{VI}}\text{O}_{10}(\text{OH})_8\text{H}_{0.03}$	5
¹ Montmorillonite	$\text{Na}_{0.4}(\text{Al}_{1.6},\text{Mg}_{0.4})\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot$	70-120
² H ⁺ -Montmorillonite	$(\text{Si}_8)^{\text{IV}}(\text{Al}_{2.90}\text{Fe}_{0.29}\text{Mg}_{0.81})^{\text{VI}}\text{O}_{20}(\text{OH})_4\text{H}_{0.81}$	103.5

¹ Bergaya et al. (2006). ² Siffert et al. (1981). Exchange capacity determined at neutrality (pH 7).

2.4.3 Selectivity coefficients

The relative affinity that a metal cation has for a soil adsorbent depends, in a complicated way, on the soil solution composition. Clay preference for one cation may be described by the law of mass action (Bergaya et al., 2006):



$$K = \frac{\{>B^+\} \times \{A^+\}}{\{>A^+\} \times \{B^+\}} \quad (6)$$

Where K represents the thermodynamic equilibrium constant and $\{>A^+\}$ and $\{>B^+\}$ represent the activities of A^+ and B^+ at the surface and $\{A^+\}$ and $\{B^+\}$ the activities of A^+ and B^+ in the equilibrium solution, respectively.

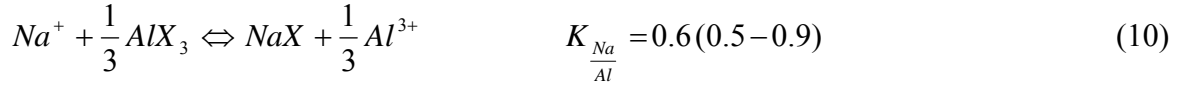
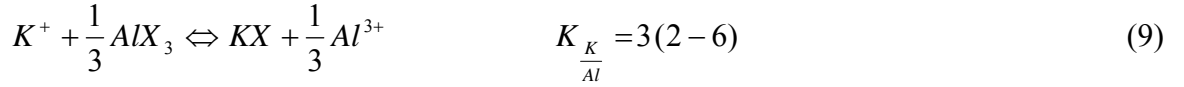
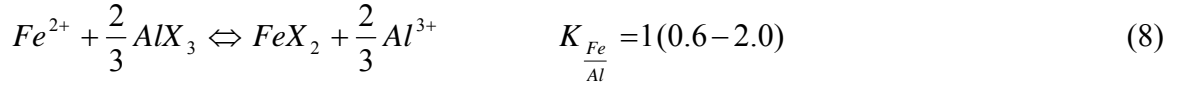
If the cation exchange is performed in sufficiently dilute solution, the activity coefficients of the ions in solution approach unity but this does not apply to the activity coefficients of the ions at the surface, which $\{>A^+\} = \gamma_A^- \times [>A^+]$ and $\{>B^+\} = \gamma_B^- \times [>B^+]$. Thus:

$$K = \frac{\{>B^+\} \times \{A^+\}}{\{>A^+\} \times \{B^+\}} = \frac{\gamma_B^- \times [>B^+] \times [A^+]}{\gamma_A^- \times [>A^+] \times [B^+]} = K_s \times \frac{\gamma_B^-}{\gamma_A^-} \quad (7)$$

Where K_s is termed the selectivity coefficient; γ_A^- and γ_B^- represent the activity coefficients of the ions at the surface; and $[>A^+]$ and $[>B^+]$ represents the concentrations of A^+ and B^+ at the surface and $[A^+]$ and $[B^+]$ the concentrations of A^+ and B^+ in the equilibrium solution, respectively.

K_s is not a true equilibrium constant but it is still a useful coefficient. However, the parameters in the selectivity coefficient can be directly measured and employed to approximate the equilibrium constant and describe ion partitioning between the adsorbed and aqueous phases. Cation exchange may be expressed by a selectivity order which refers to the ease of exchanging an existing cation in the clay surface. Generally, the selectivity order is determined by type of

exchanger in addition to type, charge and hydrated radii of replaceable cations. Nye et al. (1961) suggested that empirical exchange data is more dependant on ion pair and solution concentration than on the nature of the soil or clay. This leads to some generalizations about ion exchange in soils. Thermodynamic data for the exchange of Fe^{2+} , K^+ and Na^+ on Al-clays can be developed from compiled data (Bruggenwert and Kamphorst, 1982; Appelo and Postma, 1993) to yield:



Where bracketed selectivity coefficients were determined from reported minimum and maximum values from the compilation by Bruggenwert and Kamphorst (1982) and non-bracketed values are reported averages from the same compilation.

The differences between selectivity coefficients for the exchange of these cations and aluminum in the surface of clays suggest a selectivity order that follows a trend: $K^+ > Fe^{2+} > Na^+$. The selectivity coefficient of $K_{Na/Al} < 1$, suggests that the extent of exchange of sodium ions in solution and aluminum on the surface of clays is minor as compared to those involving K^+ and Fe^{2+} .

2.5 CLAY ACID SOILS

The relative amounts of the different cations exchangeably adsorbed by a clay soil surface (expressed as percentage of CEC) are usually referred to as (cationic) composition of the adsorption complex. Beyond the limit of 20% H/Al of cationic composition one often uses the term acid soil. Actually, the term “acid clay soils” cover a broader range from this limit up to near full saturation with H/Al. The last, occurs in exceptional circumstances like those prevailing in so-called acid-sulfate soils. The cationic composition of the adsorption complex in acid clay soils may substantially differ depending on the age of the clay. Leaching studies of aged acid clays with KCl solutions showed measurable aluminum, in addition to potassium and H^+ , concentrations in the leachates. Conversely, leaching of fresh acid clays with KCl solutions showed majorly potassium and H^+ but no aluminum concentrations in the leachates. These investigations suggested aluminum as the dominant species of the adsorption complex of aged clays. Thus, aged acid clays are H/Al-clays (Bolt, 1976).

The conversion of fresh to aged acid clays may be illustrated as follows. The fast and spontaneous H^+ attack of the octahedral layer of clay minerals results in replacement of aluminum present along the edges. The trivalent aluminum thus freed is then adsorbed preferentially in the counter ion layer of the planar sides of the clay mineral. Fresh H-clay will soon become H/Al-clay within hours at room temperature (Bolt, 1976). At the same time, such an H/Al-clay behaves like a weakly acidic exchanger, according to:



In the case of aged clays, and because of the presence of exchangeable aluminum, there is a drop of pH upon addition of a neutral electrolyte because of the release of aluminum from the surface which in turn hydrolyzes as shown in equation 11.

In aged acid clay-soils (Al/H systems), such as those which have been impacted by acid drainages, aluminum species such as Al^{3+} and the associated hydrolysis species AlOH^{2+} and $\text{Al}(\text{OH})_2^+$ and Mn^{2+} usually dominate on the surface over exchangeable H^+ . These species are released from the structure due to the acid environment surrounding the clays (Coleman, 1961). Reported average composition of the exchange phase of acidic soils (soil solution pH values below 6) from around the world, have shown Al^{3+} as the dominant species, followed by Ca^{2+} (~43% of exchangeable Al^{3+}), Mg^{2+} (~19% of Al^{3+}), Na^+ (~2.9% of Al^{3+}) and K^+ (~2.7% of Al^{3+}). Some acid soils may also contain significant amounts of exchangeable Mn^{2+} (Essington, 2004). In these soils, exchangeable aluminum may become a significant source of aluminum in the presence of strong concentrations of cations, such as Fe^{2+} , K^+ and Na^+ in the soil solution.

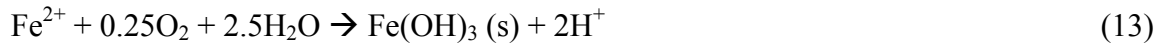
2.6 AMD CHEMISTRY

2.6.1 AMD generation

Sulfide minerals such as pyrite (FeS_2) are usually stable in a natural anoxic environment. On the other hand, in the presence of oxygen and water, pyrite quickly oxidizes, as follows (Smoke, 2007; Stumm and Morgan, 1981):



The oxidation of sulfide to sulfate solubilizes Fe^{2+} , which in turn, in the presence of oxygen, oxidizes to Fe^{3+} . At the beginning of this acidification process, at pH values over 4 and concentrations as low as 0.01 mg/L, dissolved ferric iron is unstable and undergoes hydrolysis precipitating as ferric hydroxide (Watzlaf et al., 2004; Barnes and Romberger, 1968):

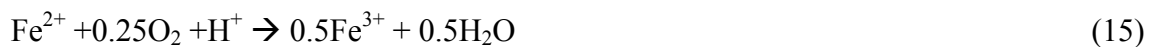


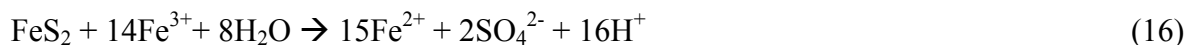
Since the net effect of these reactions is to release H^+ , which lowers the pH eventually to below 3, the solubility of the ferric ion is maintained (Silverman, 1967).

As the pH decreases below 4, the ferrous iron abiotic oxidation rate decreases dramatically as follows (Watzlaf et al., 2004; Stumm and Morgan, 1981; Singer and Stumm, 1970):

$$-\frac{d(\text{Fe}^{2+})}{dt} = k \frac{(\text{Fe}^{2+})\text{O}_{2(\text{aq})}}{(\text{H}^+)^2} \quad (14)$$

Bacteria can still play a major role in accelerating the rate of acid generation (Watzlaf et al., 2004; Beck and Brown, 1968; Duncan et al., 1967; Groudev, 1979; Silverman, 1967). In fact, these microorganisms become key at pH values below 4, assuming the main role in the oxidation of ferrous iron, Fe^{2+} to ferric iron, Fe^{3+} (Watzlaf et al., 2004; Kirby et al., 1999). Furthermore, in this pH range, dissolved ferric iron acts as an important oxidant of pyrite. At pH 2, the oxidation rate by ferric iron induced by the microbial activity is two to three orders of magnitude faster than that induced by abiotic oxidation (Adams et al., 2005). The microbial mediated reaction chemistry is well expressed by the following reactions (Watzlaf et al., 2004; Kleinmann et al., 1981; Temple and Delchamps, 1953):





Consequently, as reflected in reactions (12), (13), (15) and (16), the chemical characteristics of AMD/ARD are low pH and high concentrations of dissolved iron and sulfate. The form of iron commonly associated with subsurface anaerobic conditions is ferrous iron. Conversely, in aerobic conditions iron is frequently present as ferric iron. High concentrations of other potentially relevant dissolved metals in AMD/ARD may result due to acidic leaching through the different soil horizons. In Pennsylvania, ranges of concentrations of dissolved manganese (Mn^{2+}), 0.4-74 mg/L, magnesium (Mg^{2+}), 3.6-190 mg/L, calcium (Ca^{2+}), 3.3-410 mg/L, aluminum (Al^{3+}), 1-108 mg/L, and silicate (SiO_2), 6.4 – 67 mg/L are commonly found in AMD/ARD at pH from 2-5 (Cravotta, 2008a, b). The solubility of metals depends on the pH and redox values of AMD/ARD. Moreover bacterial activity is capable of changing the oxidation states of some metals and may indirectly influence their solubility.

Equilibrium data for aluminum, ferrous iron, potassium and sodium species found in common brackish/saline and underground environments, are presented in Table 3. Most metals exhibit an amphoteric behavior, which leads to a tendency to dissolve and form cations at low pH values or anions at high pH values (Cravotta, 2008a, b; Langmuir, 1997). Moreover, anions, such as SO_4^{2-} , may be extensively present in AMD/ARD and can form metal complexes in addition to hydroxyl ion complexes. Aluminum and iron ions tend to associate with such anions. These associations may exist due to pair formation or aqueous complexation reactions. Thus, the total concentration of soluble metals in a solution at equilibrium with a mineral can then be higher than that simply predicted by metal-hydroxide solubilities, and simple chemical equilibrium calculations (Cravotta, 2008a, b; Rose et al., 1979; Ball and Nordstrom, 1991; Langmuir, 1997; Nordstrom, 2004).

Table 3. Equilibrium constants involving speciation of Al, Fe²⁺, K⁺ and Na⁺ in AMD

Complexes	Log K	Reference
Al-hydroxyl complexes		
$\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{AlOH}^{2+} + \text{H}^+$	-5.00	May et al., 1979
$\text{Al}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	-10.1	May et al., 1979
$\text{Al}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$	-16.8	May et al., 1979
$\text{Al}^{3+} + 4\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_4^- + \text{H}^+$	-22.7	Nordstrom and May, 1996
$2\text{Al}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-7.69	Parkhurst et al., 1999
Al-sulfate complexes		
$\text{Al}^{3+} + \text{SO}_4^{2-} \leftrightarrow \text{AlSO}_4^+$	3.5	Nordstrom and May, 1996
$\text{Al}^{3+} + 2\text{SO}_4^{2-} \leftrightarrow \text{Al}(\text{SO}_4)_2^-$	5.0	Nordstrom and May, 1996
Fe-sulfate complexes		
$\text{Fe}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{FeSO}_4$	2.25	Parkhurst et al., 1999
$\text{Fe}^{2+} + \text{HSO}_4^- \leftrightarrow \text{FeHSO}_4^+$	1.08	Parkhurst et al., 1999
Fe-hydroxyl complexes		
$\text{Fe}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}^+ + \text{H}^+$	-9.50	Parkhurst et al., 1999
Fe-chloride complexes		
$\text{Fe}^{2+} + \text{Cl}^- \leftrightarrow \text{FeCl}^+$	0.14	Parkhurst et al., 1999
K-sulfate complexes		
$\text{K}^+ + \text{SO}_4^{2-} \leftrightarrow \text{KSO}_4^-$	0.85	Parkhurst et al., 1999
Na-sulfate complexes		
$\text{Na}^+ + \text{SO}_4^{2-} \leftrightarrow \text{NaSO}_4^-$	0.7	Parkhurst et al., 1999

2.6.2 The iron solubility in AMD

The field data from 140 abandoned coal mines in Pennsylvania showed ferrous iron as the dominant species of iron in AMD in the pH range from 2.6 to 7.3, with ferric species present at low concentrations (Cravotta, 2008a, b). The ferric ion is mostly dissolved only under strongly acidic conditions ($\text{pH} < 2$). Above $\text{pH} > 2$, ferric iron is usually hydrolyzed and precipitated as different ochreous minerals such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) ($\text{pH} \sim 2$), schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4) \cdot n\text{H}_2\text{O}$) ($\text{pH} 2.5\text{--}4$), or ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) ($\text{pH} > 5$) (Letcher, 2007). On the other hand, the ferrous iron solubility under $\text{SO}_4^{2-} < 2000 \text{ mg/L}$ and $\text{pH} < 8$ is not controlled by hydroxide-mineral solubility or by SO_4^{2-} complexation. Thus, it is more soluble than ferric iron remaining in solution below $\text{pH} \sim 8$ (Cravotta, 2008a, b).

The Fe^{2+} activities in AMD from 140 abandoned mines in Pennsylvania were evaluated by Cravotta (2008a, b). These evaluations were determined with the use of chemical speciation software (WATEQ4F) using measured information of dissolved Fe, eH (redox potentials) and temperature. This information was presented on pH-pC diagrams. The theoretical solubility of Fe^{2+} at equilibrium with OH^- , and CO_3^{2-} minerals were also computed and plotted as reference lines on the same diagram. The Fe^{2+} levels in these AMD sites were lower than the theoretical solubilities of Fe^{2+} at equilibrium with these (OH^- , and CO_3^{2-}) minerals at $\text{pH} < 5$. This suggests that ferrous iron in AMD can be retained within the subsurface environments where it is commonly generated.

2.6.3 The aluminum solubility in AMD

The aluminum released from Al-bearing minerals to the pore water may undergo hydrolysis and complexation with preference with SO_4^{2-} and less so with Cl^- . These interactions result in Al-hydroxyl, Al-sulfate and Al-chloride compounds. In absence of SO_4^{2-} and Cl^- , the speciation of aluminum is described by its equilibrium with hydroxides at various pH values. At pH values less than 4, aluminum occurs as Al^{3+} (Eaton et al., 2005). As pH increases beyond 4, Al undergoes hydrolysis (Nordstrom and May, 1996) to form a series of Al-hydroxyl compounds. Moreover, as pH increases beyond 4, aluminum experiences a decrease in solubility. At the neutral pH range (6-8), where $\text{Al}(\text{OH})_3$ and aluminosilicate minerals have their minimum of solubility, aluminum is relatively insoluble (Nordstrom and Ball, 1986; Bigham and Nordstrom, 2000). Eventually, above neutral pH values ($\text{pH} > 7$), the predominant form of dissolved aluminum is the ion complex $\text{Al}(\text{OH})_4^-$.

The formation of Al-chloride compounds is minor; however, aluminum complexation with sulfate in solution is significant (Sposito, 1995). The formation of aluminum sulfate complexes as ion pairs, outer-sphere and inner sphere complexes was reported by Nordstrom and May (1996). The distribution of these forms is temperature, pH and ligand-concentration dependent (Akit et al., 1985). These complexes are dominant at low pH values and high sulfate concentrations (Driscoll and Postek 1996). Consequently, Al may tend to associate with sulfate in AMD/ARD depending on the AMD/ARD conditions. The predominant Al- SO_4 complex is AlSO_4^+ at low SO_4^{2-} concentrations and becomes $\text{Al}(\text{SO}_4)_2^-$ at higher SO_4^{2-} concentrations (Driscoll and Postek 1996).

The aluminum activities in AMD from 140 abandoned mines in Pennsylvania were evaluated by Cravotta (2008a, b). These evaluations were performed with the use of chemical speciation software (WATEQ4F). The information from these evaluations was presented on pH-pC diagrams. The theoretical solubility of Al at equilibrium with amorphous ($\text{Al}(\text{OH})_3$), allophane ($[\text{Al}(\text{OH})_3]_{(1-x)}[\text{SiO}_2]_{(x)}$ (where $x = 1.24-0.135$ pH) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) were also computed and plotted as reference lines on the same diagram. The Al levels in these AMD sites were undersaturated with respect to the theoretical solubilities of Al at equilibrium with these minerals; amorphous ($\text{Al}(\text{OH})_3$), allophane ($[\text{Al}(\text{OH})_3]_{(1-x)}[\text{SiO}_2]_{(x)}$) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$); at $\text{pH} < 4$. This suggests that clays, such as kaolinites, could be sources of elevated Al in AMD at $\text{pH} < 4$. The exchange of ferrous iron in AMD with Al in the clay surface would explain and is consistent with the elevated Al observed in some AMD/ARD discharges at $\text{pH} < 4$.

2.7 IRON SORPTION BY CLAYS

The sorption capacities of kaolinite or smectite clays are widely documented in the literature (Fordham, 1973; Angove and Johnson, 1997; Schindler, 1987; Spark, 1995; Sposito et al, 1983a, b; Charlet et al., 2005). Nevertheless, despite of the significance of ferrous iron in natural reduced environments, the sorption of ferrous species in AMD/ARD and its effects on the release of aluminum on clay minerals has not been documented. The following are the major literature findings on the sorption properties of kaolinite and smectite clays.

2.7.1 Kaolinite sorption capacity

Literature regarding the sorption of ferrous iron on kaolinite has not been found. The sorption of the oxidized form of iron, Fe^{3+} , on kaolinite was investigated by Fordham (1973) at various temperatures (2°C, 20°C and 40°C) and at constant and variable pH values in the range of 2-4.5. He showed that iron was sorbed reversibly at some sites and strongly at others. Leaching of kaolinite with strong concentrations of unhydrolyzed trivalent and divalent ions did not release iron from the clay. Based on these results and a slower reaction than expected, he suggested that the reversible reaction was not a simple ion exchange. Extraction studies supported the existence of strongly bound iron. He hypothesized that this strong sorption could result from chemical combination with unsaturated oxygen atoms at the edges of the clay lattice. In such a case, iron ions being sorbed at sites suitable located relative to each other could form low-order polymers. Each one of these units would remain firmly attached to the clay. However, his attempts to define the location of sorbed iron by the use of reagents capable of reacting with either the basal surfaces or the edges of kaolinite particles failed to give conclusive results.

Studies of sorption of other divalent cations on kaolinite, such as Cu^{2+} , Cd^{2+} and Pb^{2+} , have generally agreed that sorption of these cations on kaolinite involves two kinds of binding sites: weakly acidic XH sites able to undergo ion exchange, and AlOH sites on which specific sorption occurs through the formation of inner sphere complexes (Schindler, 1987). Because the first stage of sorption of Zn^{2+} , Co^{2+} , Cu^{2+} and Cd^{2+} on kaolinite began at the same pH for all four metals, Spark (1995) deduced that the weakly acidic groups of Schindler (1987) were the permanent negatively-charged sites of the siloxane faces. Kaolinite has been reported by Giese et al. (2002) as a clay mineral with no ionic substitution and therefore a negligible layer charge and

elements between the layers. However, it is accepted that the siloxane surface carries a small negative charge that is almost independent of pH (Chukwudi, 2008). Although it is difficult to insert materials, in general, small highly polar organic molecules can insert kaolinite. In addition to this molecular species, certain inorganic salts also can be introduced between the 1:1 layers (sometimes called intersalates). None of these intercalates or intersalates has been recognized in natural mineral deposits.

2.7.2 Smectite sorption capacity

Several studies have pointed a great selectivity of divalent cation-chloride ion pairs for exchange positions in the smectite interlayer (Fletcher and Sposito, 1989; Tournassat et al., 2004a). The exchange of Fe^{2+} with other cations such, as Na or Ca, on the surface complex of smectite clays has been previously reported by Charlet et al. (2005) and Lantenois et al. (2005). Charlet et al. (2005) conducted their experiments in Cl^- anionic media and at low pH values from 2.1 to 3.6, in order to prevent specific sorption at the edges of the platelets and promote cation exchange adsorption of ferrous species. Solution and exchange speciation computations, under these experimental conditions, suggested that ferrous iron was the predominant iron species in the solution; meanwhile FeCl^+ species were dominant in the Fe^{2+} exchanged clay.

A conceptual model proposed by Lantenois et al. (2005) explained the destabilization of dioctahedral smectites as a result of their interaction with metallic iron at realistic temperatures in the context of nuclear waste disposal (80°C). This model relies on the existence of high (basic) pH conditions that result in the deprotonation of OH-groups in smectite and further oxidation of Fe^0 to Fe^{2+} (Fe^0 acting as a proton acceptor). This step is followed by sorption of Fe^{2+} cations on

the edges of smectite particles which present high affinity for this cation (Charlet et al., 2005; Lantenois et al., 2005).

2.8 CONCLUSIONS DRAWN FROM LITERATURE REVIEW

1. Clays are common products of the weathering of silicate minerals that play a significant role on the release of cations from clay soils to the pore water solution.
2. In the absence of organic forms, the release of aluminum from AMD/ARD-affected clay soils is due to ion exchange and clay dissolution processes.
3. Long-term AMD impacted clay soils are H/Al saturated, with the H/Al ratio in the adsorption complex close to 100% their cation exchange capacities.
4. The dominant species on the exchange solid phase of aged acid clays, such as those impacted by AMD/ARD, is commonly aluminum.
5. Other significant species on the exchange solid phase of aged acid clays include Ca^{2+} , Mg^{2+} , Na^+ , K^+ and Mn^{2+} .
6. Smectite clays are the most common phyllosilicates in soils and sediments.
7. Smectite clays have much higher CEC than kaolinite clays.
8. Smectite clays are easily degraded under acidic conditions and their proton-promoted dissolution often results in more stable forms of clays, such as kaolinites.
9. Fe^{2+} , K^+ and Na^+ concentrations in brackish/saline and underground AMD/ARD at pH between 2 and 3 have the potential to exchange with aluminum on the surface of H/Al-clays.
10. The selectivity coefficients for the exchange of K^+ , Fe^{2+} and Na^+ with aluminum in the surface of clays suggest the selectivity order: $\text{K}^+ > \text{Fe}^{2+} > \text{Na}^+$.

11. The observed low Fe^{2+} levels in field AMD as compared to the theoretical solubilities of Fe^{2+} at equilibrium with common OH^- and CO_3^{2-} minerals found in AMD sites suggest the possibility that Fe^{2+} in AMD is retained within subsurface environments.
12. Clays have the potential to sorb ferrous iron in AMD and thus retain it in the subsurface environments where AMD is commonly generated.
13. The elevated Al levels observed in some AMD/ARD discharges at $\text{pH} < 4$ is consistent with the exchange of ferrous iron in AMD with Al in the clay surface.

A wide variety of studies have investigated the mechanisms and factors involved on the release of aluminum from Al-bearing clays when exposed to acidic and saline conditions. Their findings can not be fully applied to different leaching solutions such as acid mine/rock drainages. Thus, the phenomena leading to the generation of elevated aluminum levels in AMD/ARD is not completely understood. A better understanding of the factors and mechanisms involved in the release of high amounts of aluminum from these AMD-ARD-affected clays is critical and fundamental information is needed to consider alternative remediation strategies for AMD/ARD with elevated concentrations of Al.

3.0 METHODS AND MATERIALS

The leaching experiments in this study were conducted in two phases: phase 1 (preliminary studies) and phase 2 and at room temperature, 25°C. The phase 1 (preliminary experiments) included short- and long-term leaching of smectite clays. The leaching solutions used in the leaching of these clays were synthetic acid drainages typically found in the field. Short-term leaching experiments of kaolinite clays and ARD-impacted clay soil from a Centre County site, PA with these acid drainages were conducted as well. Based on the information developed from the experiments in phase 1, phase 2 focused on the long-term leaching of smectite clays. The leaching experiments in phase 2 were conducted at a broader range of pH values and metal (ferrous iron, potassium and sodium) concentrations in the synthetic acid drainages. Thus, the outcome of this study can be applied to a wider spectrum of AMD/ARD affected sites.

The field clay soil used in this study was collected downstream the main source of pollution of an aluminum-containing ARD affected site in Center County, PA (Jonathan Run site). The smectite clay used in this study was sodium-saturated bentonite, which is mostly montmorillonite (dioctahedral smectite), supplied by Fisher Scientific (Pittsburgh, PA). Finally, acid-washed kaolinite, $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$, was provided by Fisher Scientific (Pittsburgh, PA) as well.

3.1 PHASE 1 LEACHING (PRELIMINARY EXPERIMENTS)

3.1.1 Long-term leaching of smectites with conventional acid drainages

In these long-term leaching experiments, a smectite mixture in a batch reactor simulated leaching of smectite clays with conventional and synthetic acid drainages. By conventional acid drainage it is meant AMD/ARD containing initial ferrous iron concentrations of around 500 mg/L at pH 3 and frequently found in AMD/ARD affected sites.

Pretreatment of smectite

The smectite supplied by Fisher Scientific (Pittsburgh, PA), was pre-treated and acidified before use in leaching experiments to approach smectite conditions found in AMD/ARD affected sites. A predetermined quantity of this smectite (225 g) was slurried with 11 ml of 12.1N HCl and deionized (DI) water, resulting in 2 L of smectite stock suspension at around pH 3.0 with the composition shown in Table 4.

Preparation of stock leaching solutions

Measured quantities of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2SO_4 were used to prepare synthetic ARD and sulfuric acid stock leaching solutions with the measured compositions shown in Table 4.

Theoretical initial chemical composition of smectite mixtures in reactors

The chemical compositions of synthetic ARD and sulfuric acid stock leaching solutions (Table 4) were chosen to obtain desired initial chemical compositions of smectite mixtures in the reactors (at leaching time of zero hours) (Table 5). For this purpose, two 2-L Erlenmeyer flasks were used as reactors to conduct the experiments. A sketch of the system of reactors is shown in Figure 3. Known volumes of smectite stock suspension (830 mL) were added to each reactor. Synthetic ARD and sulfuric acid stock leaching solutions (970 mL) were subsequently added to each reactor, resulting in 1,800 mL suspensions containing 93.4 g of smectite in each reactor. The resultant wt/wt (g/g) clay to solution ratio in the reactors was 1:20. The election of this clay:solution ratio was made in order to obtain detectable aluminum concentrations, determined by flame atomic absorption spectrometry (AAS), in the smectite-ARD mixture. The smectite-ARD mixture was prepared to simulate leaching of smectite clays with conventional ARD containing initial ferrous iron concentrations of around 500 mg/L at pH of 3. On the other hand, the smectite-sulfuric acid mixture was prepared to have an initial pH of 3, as shown in Table 5. The solid phases in the reactors were maintained in suspension by means of magnetic stirrers. An inert atmosphere was maintained throughout the experiments by means of a N₂ blanket within the reactors to minimize the oxidation of ferrous iron.

Table 4. The composition of stocks of smectite suspension and leaching solutions in long-term leaching experiments of smectite with conventional acid drainages (phase 1)

Prepared synthetic stocks	pH	¹Al(mg/L)	Fe (mg/L)	Na⁺ (mg/L)
Smectite stock suspension	3.0	2	11	956
Sulfuric acid solution	3.1	2<1	² <1	2.3
ARD	3.3	2<1	948	2

¹ Determination of aluminum from non-digested filtered extracts. ² Below practical quantitation limit (PQL) of 1 mg/L.

Table 5. Theoretical initial compositions of smectite mixtures in the reactors in long-term leaching experiments of smectite with conventional acid drainages (phase 1)

¹Initial composition of mixtures Wt/wt clay to solution ratio: 1/20	pH	Al(mg/L)	Fe (mg/L)	Na⁺ (mg/L)
Smectite-Sulfuric acid mixture	3.1	<1	5	442
Smectite-ARD mixture	3.1	<1	516	442

¹Theoretical determination of initial composition of smectite mixtures in reactors based on compositions of prepared smectite stock suspension, synthetic leaching solutions and mixed volumes in reactors.

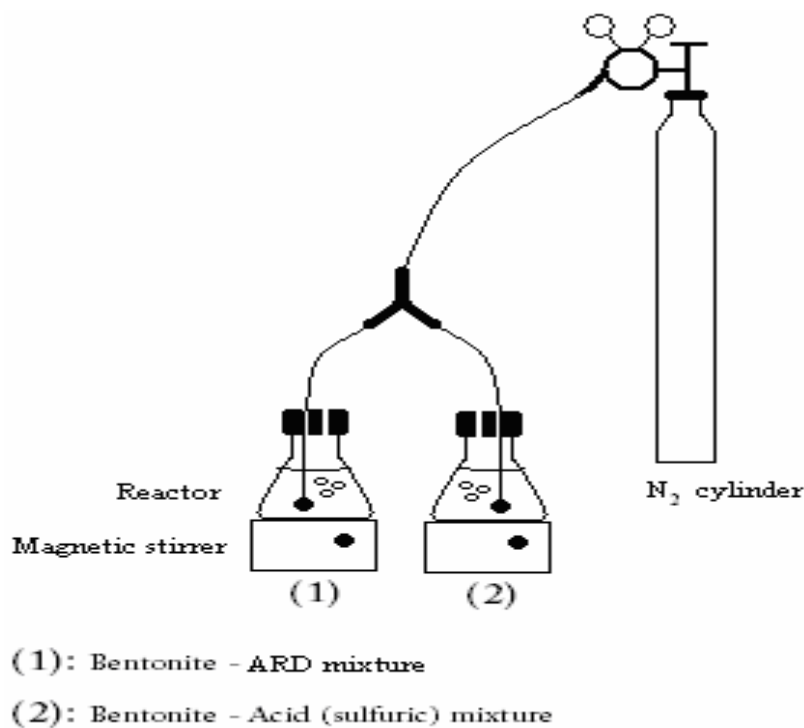


Figure 3. System of 2 liter batch reactors and magnetic stirring

3.1.2 Short-term leaching of smectites, kaolinites & field clay soil with brackish acid drainages

The kaolinite and field clay soil used in these leaching experiments were acid clays. Thus, these clays required no further chemical pretreatment to approach clay conditions typically found in AMD/ARD affected sites. These short-term leaching experiments involved leaching of smectite and kaolinite clays as long as field clay soils. Synthetic leaching solutions used in these experiments included brackish acid drainages frequently found in AMD/ARD affected sites.

Pretreatment of smectite:

Pretreatment of smectite was conducted in a different fashion than that described in the previous sub-section. This new procedure allowed for the determination of the experimental initial conditions as compared to the previously determined theoretical initial conditions in the reactors. Furthermore, this procedure allowed for the preparation of H/Al saturated smectites that better approaches clay conditions found in AMD/ARD affected sites.

A predetermined amount (60 g) of the smectite supplied by Fisher Scientific (Pittsburgh, PA) was added to 1 L of 0.05 N HCl. During the stirring of this suspension, an additional 4 mL of 12.1 N HCl was added to stabilize the pH over time. After the pH became stable, the suspension was concentrated by heating it. The concentrated suspension was cooled at room temperature, 25°C, transferred to centrifuged tubes and centrifuged at 8,500 G for 15 minutes in a Fisher Scientific AccuSpin Model 400 Benchtop Centrifuge.

After centrifugation, supernates were collected and pH, sodium, and total aluminum concentrations were determined by flame atomic absorption spectrometry (AAS). Then, 30 mL of 0.05 N HCl were added to the remainder of the clay in the 50 mL centrifuge tubes and the mixture was shaken for 1 minute to keep the clay in suspension. After that, the tubes were centrifuged a second time and the pH, sodium, and total aluminum concentrations were measured again. The procedure was repeated until the sodium concentration in the supernatant was below 5 mg/L. After that, the same procedure was repeated 3 more times with distilled water to minimize excess sodium and aluminum in the pore water.

Preparation of stock leaching solutions

The chemicals used in the preparation and the measured chemical composition of synthetic stock leaching solutions are shown in Table 6. The leaching solution labeled sulfuric acid was prepared adding 2.7 mL of 0.36N H_2SO_4 to 2 L of deionized water. A predetermined volume (1 L) of this solution was transferred to a different glass beaker, where 2.5 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added to prepare the ARD 1 leaching solution. Finally, a predetermined volume of ARD 1 (500 mL) was transferred to a third glass beaker, where 0.48 g of KCl and 1.3 g of NaCl were added to prepare ARD 2.

Experimental initial chemical composition of clay mixtures in reactors

The initial chemical composition of the clays mixtures in each reactor (at leaching time of zero hours) equals the chemical composition of the stock leaching solutions used in these experiments (Table 6). The leaching experiments were conducted in 50 ml batch reactors at gram/gram (wt/wt) clay to stock solution ratios of 1:10 (10% wt/wt). The predetermined amounts of clay were mixed with calibrated volumes of 3 different prepared synthetic stock solutions: sulfuric acid solutions (labeled ‘sulfuric acid’), a leaching solution simulating underground ARD (labeled ‘ARD 1’), and a third leaching solution simulating underground and brackish ARD (labeled ‘ARD 2’), as shown in Table 6.

The reactors in these experiments were continuously shaken to maintain the solid phase in suspension by means of an orbital shaker. The system of reactors used in this experiment is shown in Figure 4. This experimental approach facilitates contact between clay particles and leaching solutions and provides adequate stirring energy to better increase kinetics, optimizing reactions times, while minimizing the effect of film diffusion on the rates of aluminum release.

All batch experiments were carried out in duplicate. Samples were collected after 67 hours of reaction time. Based on the experimental results from the long-term leaching of smectite with conventional acid drainages, leaching times in this set of experiments lasted around 70 hours. Leaching times of 70 hours are sufficiently close to the apparent steady-state point for purposes of quantifying the release of aluminum from the surface of these clays after interaction with the different leaching stock solutions shown in Table 6.

Table 6. The compositions of stocks of leaching solutions in short-term leaching experiments of smectite, kaolinite and field clay soil with brackish acid drainages (phase 1)

*Prepared synthetic stocks	Chemical reagents used	pH	⁴Total Al	Fe²⁺	K⁺	Na⁺
Sulfuric Acid	H ₂ SO ₄	2.6 – 2.7	¹ <1	² <2	² <2	³ <5
ARD 1	H ₂ SO ₄ , FeSO ₄ 7H ₂ O	3.1 – 3.2	¹ <1	506 - 673	² <2	³ <5
ARD 2	H ₂ SO ₄ , FeSO ₄ 7H ₂ O, NaCl, KCl	3.3 – 3.4	¹ <1	518 - 621	511 - 568	821 - 992

*All concentrations in mg/L. ¹Below practical quantitation limit (PQL) of 1 mg/L. ² Below PQL of 2 mg/L. ³ Below PQL of 5 mg/L. ⁴Determination of aluminum with non-digested samples.

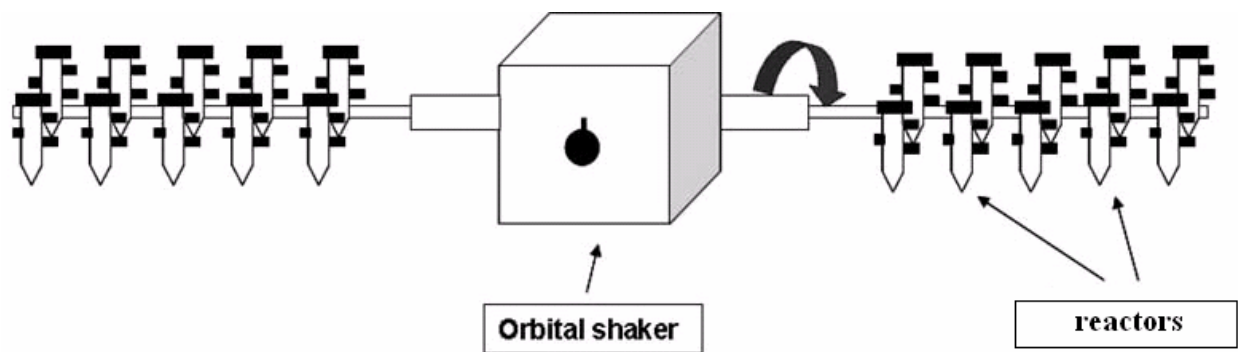


Figure 4. System of batch reactors and orbital shaking

In these short-leaching experiments there was no need to maintain anoxic conditions within the batch reactors in order to minimize the oxidation of ferrous iron. The determination of ferrous iron concentrations in stock leaching solutions showed that over 98% of the initial iron remained in the ferrous form after more than 67 hours. This was expected since the pH of the stock solutions was in the range of 3.1 to 3.4. The colorless 67 hour supernatants observed after centrifugation implied an absence of $\text{Fe}(\text{OH})_3$, which is consistent with these results. Consequently, Fe^{3+} can be considered a minor component in the total iron concentrations (Fe^{2+} and Fe^{3+} species) determined by AAS.

3.2 PHASE 2 LEACHING

Pretreatment of smectite

The smectite supplied by Fisher Scientific (Pittsburgh, PA), was pre-treated and acidified before use in leaching experiments following an equivalent pretreatment procedure to that mentioned in the last sub-section. This procedure allows for the preparation of H/Al saturated smectites that better approaches clay conditions in AMD/ARD impacted sites.

Preparation of synthetic stock leaching solutions

The synthetic stock leaching solutions used in these experiments were:

- Sulfuric acid solutions labeled as “sulfuric sol.” and prepared to have initial pH values of 2 and 3 to investigate the proton-promoted dissolution of these clays.
- Leaching solutions labeled as “AMD1”, and prepared to have ferrous iron concentrations of around 500 mg/L (AMD1_500) and 1000 mg/L (AMD1_1000) at initial pH values of 2 and 3, simulating conventional underground AMD.
- Leaching solutions labeled as “AMD2_500” and prepared to have ferrous iron concentrations of around 500 mg/L, sodium concentrations of around 1000 mg/L and potassium concentrations of around 500 mg/L at initial pH values of 2 and 3, simulating underground and brackish AMD.
- Leaching solutions labeled as “AMD2_50000” and prepared to have ferrous iron concentrations of around 500 mg/L, sodium concentrations of around 50000 mg/L and

potassium concentrations of around 50000 mg/L at initial pH values of 2 and 3, simulating saline/brine AMD that can be generated in the extraction process used to tap tight shale reserves (such as could be the case of the Marcellus shale formation in Pennsylvania.)

- Deionized water used as a control.

The chemical reagents and their amounts used in the preparation of these synthetic stock solutions are shown in Table 7. The chemical compositions of these leaching solutions as measured by AAS are summarized in Table 8.

Table 7. The chemical reagent amounts used to prepare the stocks of leaching solutions in leaching experiments of smectite with brackish and saline acid drainages (phase 2)

	Chemical reagents used					
Prepared synthetic stocks	D.W. (mL)	0.36 N H₂SO₄ (mL)	0.0121 N HCl (mL)	FeSO₄·7H₂O (g)	KCl (g)	NaCl (g)
Initial pH 2						
Deionized water (D.W.)	250	---	---	---	---	---
Sulfuric acid	230	20	---	---	---	---
AMD1_500	230	20	---	0.63	---	---
AMD1_1000	230	20	---	1.25	---	---
AM2_500	230	20	---	0.63	0.24	0.64
AMD2_50000	230	5	---	0.63	23.9	31.8
Initial pH 3						
Prepared Synthetic Stocks	D.W. (mL)	0.0036 N H₂SO₄ (mL)	0.0121 N HCl (mL)	FeSO₄·7H₂O (g)	KCl (g)	NaCl (g)
Sulfuric acid	230	20	---	---	---	---
AMD1_500	230	20	---	0.63	---	---
AMD1_1000	225	20	5	1.25	---	---
AM2_500	220	20	10	0.62	0.24	0.64
AMD2_50000	220	20	10	0.62	23.8	31.8

Table 8. The compositions of stocks of leaching solutions in leaching experiments of smectite with brackish and saline acid drainages (phase 2)

Prepared synthetic stocks	pH	^{1,2} Total Al	^{1,2} SiO ₂	¹ Fe	¹ K	¹ Na	¹ Ca	¹ Mg	¹ Mn
Initial pH 2									
Deionized water (D.W.)	5.7	<1	<5	<2	<2	4.2	13.5	<2	<2
Sulfuric acid	2.1	<1	<5	<2	<2	<2	<2	<2	<2
AMD1_500	2.1	<1	<5	583	<2	<2	<2	<2	<2
AMD1_1000	2.1	<1	<5	1142	<2	<2	<2	<2	<2
AM2_500	2.0	<1	<5	583	420	795	2.2	<2	<2
AMD2_50000	2.1	<1	9.7	480	45291	45805	<2	<2	<2
Initial pH 3									
Sulfuric acid	2.8	<1	<5	<2	<2	<2	3.7	<2	<2
AMD1_500	3.2	<1	<5	559	<2	2.6	4.5	<2	<2
AMD1_1000	3.1	<1	<5	1132	<2	<2	2.9	<2	<2
AM2_500	3.2	<1	<5	548	448	851	2.9	<2	<2
AMD2_50000	3.1	<1	7	434	45111	48758	20.8	<2	<2

¹Practical quantitation limits (PQL) were: 1 mg/L for Al, 2 mg/L for Fe, K, Na, Ca, Mg and Mn; 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples.

Experimental initial chemical composition of smectite mixtures in reactors

The initial chemical composition of the clays mixtures in each reactor (at leaching time of zero hours) equals the chemical composition of the stock leaching solutions used in these experiments (Table 8). A series of predetermined amounts of prepared H/Al-smectite clay (0.25 g) were mixed with 20 ml of different stock leaching solutions (Table 8) and shaken overtime during about 2 months in 20 ml batch reactors, by means of an orbital shaker as previously shown in Figure 4. An inert atmosphere of N₂ gas was injected within each one of these batch reactors to minimize the oxidation of ferrous iron in leaching solutions. In each series, each one of the batch reactors was collected and sacrificed at predetermined amounts of time.

The chemicals used for the preparation of synthetic stock solutions in this study were reagent grade. Acid-washed kaolinite, (Al₂Si₂O₅(OH)₄) was used in powdered form. Prepared H/Al-smectite and field clay soil were dried overnight at 105°C, gently ground, and sieved using a #20 mesh, before being used in the batch experiments.

3.3 SAMPLE COLLECTION, PRESERVATION AND ANALYSIS

In the long-term leaching experiments of phase 1 (lasting over 1000 hours of leaching), the samples were collected after predetermined reaction times and monitored for dissolved oxygen (Orion O₂ electrode Model 97-08-00). The O₂ content in the samples was repeatedly observed to be around 1.6±0.7 mg/L with pH values from around 3 to 3.4 (Smectite-ARD mixture). The O₂ content in the samples from phase 2, increased overtime up to values of 3 mg/L (Appendices A-

B) with pH values varying from around 2 to 3. The colorless supernatants observed after centrifugation implied an absence of $\text{Fe}(\text{OH})_3$ which is consistent with the low concentrations of O_2 and low pH values within the batch reactors. Consequently, Fe^{3+} can be considered minor species in the total iron concentrations (Fe^{2+} and Fe^{3+} species) determined by AAS.

The samples were consequently transferred to centrifuge tubes and centrifuged at 8,500G for 15 minutes in a Fisher Scientific AccuSpin Model 400 benchtop centrifuge (phase 1) and at 340 rpm for 15 minutes in a Fisher Scientific Centrifuge Model 228 Benchtop Centrifuge (phase 2) respectively, to separate the clays from the aqueous portion. The pH was measured after centrifugation using a previously calibrated Fisher Accumet 25 benchtop electrode pH meter equipped with a Fisher Scientific Accumet pH electrode. Subsequently, the supernates were filtrated through 0.45 μm HA IsoporeTM membrane filters supplied by Millipore and transferred to 15 ml centrifuge tubes. The filtered extracts in these 15 ml centrifuge tubes were acidified with 2 to 3 drops of 15.8N HNO_3 to a pH below 2 to minimize precipitation and adsorption on container walls. The samples were stored at 4°C for further analysis.

Experiments run until steady-state conditions were approached. Short-term leaching experiments were conducted during 67 hours of leaching time. These experiments focused on cation exchange between iron, potassium and sodium in synthetic leaching solutions and aluminum on the surface of the clays. The exchange reactions are typically fast, of the order of hours. Thus, these leaching times below 100 hours (67 hours) were considered sufficient to approach steady-state conditions for the purpose of investigating cation exchange reactions. Experimental results from long-term leaching experiments supported the election of these leaching times in short-leaching experiments.

In long-term leaching experiments, the experiments were considered close to steady-state when the levels of aluminum in at least three consecutive samples taken at least 1 week apart approached an asymptotic value and were within 10% of the highest aluminum level.

The concentrations of total aluminum, iron, potassium, sodium, silica, calcium, magnesium and manganese were determined by AAS (Standard Methods 2005). Prior to heavy metal analysis, the filtered extracts were digested with concentrated HNO_3 and HCl in a CEM-MARS microwave digester.

The total dissolved aluminum (mg/L) leached from predetermined quantities (g) of H/Al-smectite, kaolinite and clay soil from Centre County, PA after 67 hours of leaching with different synthetic solutions is shown in Figure 5. In this figure, the y-axis represents dissolved aluminum concentrations from microwaved digested leachates while the x-axis shows dissolved aluminum concentrations from non-digested leachates. The data in Figure 5 shows a fair 1:1 correlation between dissolved aluminum from non-digested and microwaved digested extracts as implicit by the regression equation, $y=1.0148x+0.1953$ and the regression coefficient $R^2=0.9982$. Thus, aluminum concentrations determined from non-digested extracts yields data of defensible quality. Therefore, determination of aluminum concentrations from both microwave digested and non-digested filtered extracts showed equal results. Thus, microwave digestion for aluminum and silica in leachate samples was discontinued. Thus, dilution of samples associated with the addition of digestion acids was prevented while the detection ability of these elements was enhanced. Samples of each leachate were analyzed in triplicate. Resultant analyses were averaged.

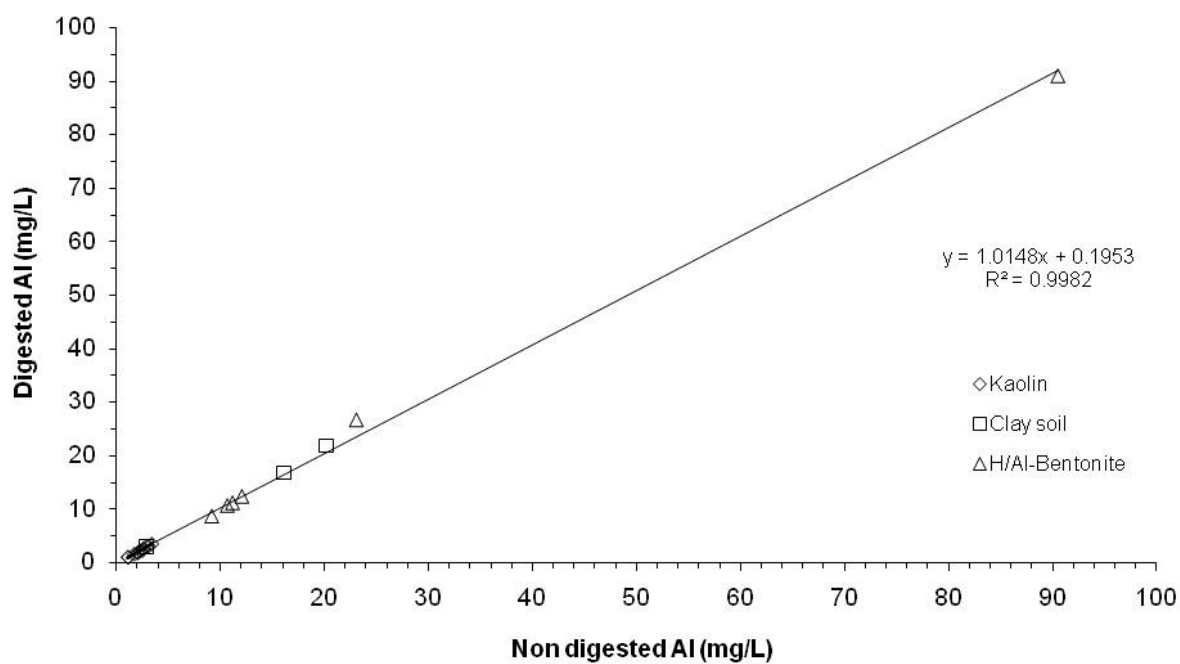


Figure 5. Aluminum concentrations in non digested vs microwaved digested filtered extracts

4.0 RESULTS AND DISCUSSION

4.1 PHASE 1 LEACHING (PRELIMINARY STUDIES)

4.1.1 Long-term leaching of smectites with conventional acid drainages

The release of aluminum from smectite clays leached with synthetic ARD and sulfuric acid leaching solutions was evaluated. The exchange of ferrous iron with aluminum in the surface of smectite clays was explored. The results from leaching experiments suggested that ion-exchange and clay dissolution were the main processes dominating the release of aluminum from smectite clays when leached with acid rock drainages. The results from batch laboratory leaching of smectite clays with synthetic acid rock drainages were compared with historical data from the Jonathan Run site and showed agreement with the observed evolution of Al and low iron concentrations in ARD from the Centre County pyritic sandstone and shale fill at the Jonathan Run site (Vazquez et al. 2011).

Jonathan Run site description

Jonathan Run is a tributary to the South Fork of Beech Creek, located near the intersection of State Route 144 and I-80 in Centre County, Pennsylvania. The headwaters of Jonathan Run are located east of Snow Shoe in Centre County, Pennsylvania. It was once a quality stream used as a trout fishery for the local public and was used to support breeding ponds for the Snow Shoe Summit Lodge Corporation. The stream was seriously degraded in the 1960's during the construction of Interstate 80. The headwaters area was filled and used for staging during the highway's construction. A large amount of excess sandstone, produced by several large road cuts, was piled on the site. The same sandstone was used to construct a 60-80 foot high embankment that supports both lanes of I-80.

After the construction of I-80 in the 1960's by the Pennsylvania Department of Transportation (PennDOT), Jonathan Run was no longer able to support aquatic life. Prior research determined that the primary source of contamination was due to acidic sandstone fill that was placed across the stream valley to support the interstate. The interstate platform, which was built directly over the stream channel, was all constructed using outcrops from nearby road cuts that contained high amounts of sulfide in the form of pyrite. The Jonathan Run stream was allowed to flow through a concrete culvert constructed under the embankment of the I-80. A sketch of the Jonathan Run area besides the culvert is shown in Figure 6. When these minerals are exposed to oxygen and water they oxidize and generate acidity. The acidic discharge in Jonathan Run contains high aluminum and low iron concentrations which is different from other acidic drainages. It is assumed when the acidic water runs over the alumino-silicate (clay) soil,

the clay is dissolved and aluminum (Al^{3+}) is replaced by hydrogen ions (H^+). The aluminum is toxic to aquatic life, because of its ability to clog the gills of fish.

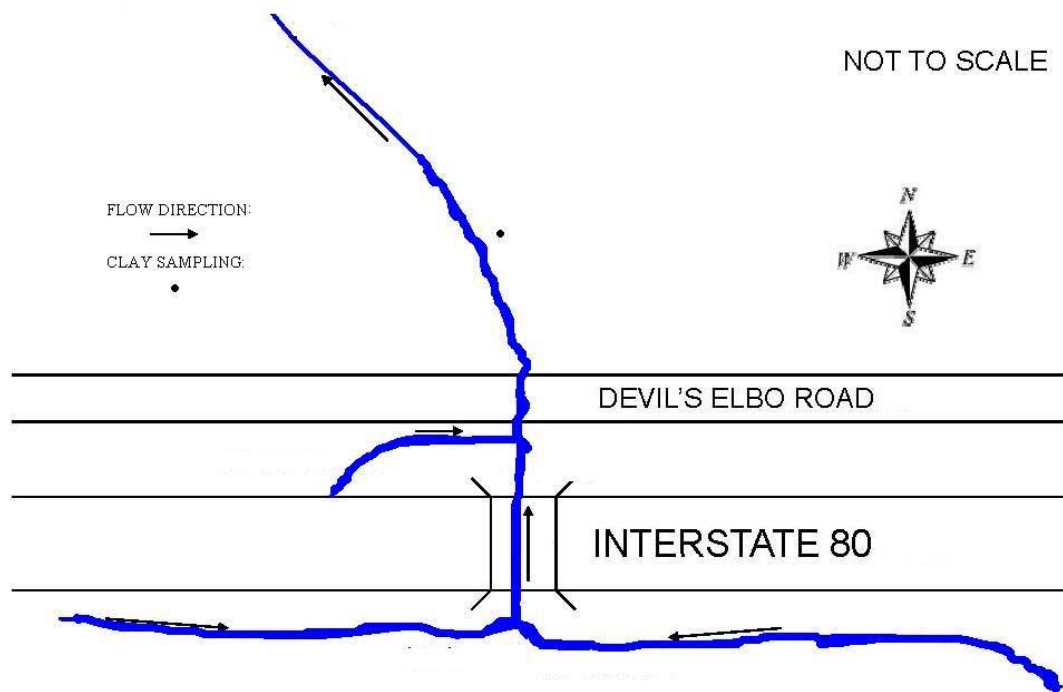


Figure 6. The sketch of the Jonathan Run site besides the culvert of the I-80 embankment

Historical data at the Jonathan Run site

The quarterly averaged aluminum concentrations from the major surface seep at the Jonathan Run site and measured during the time frame 1999 to 2008 appear to follow two different trends; from 1999-2003 and from 2003-2008, as shown in Figure 7. The averaged aluminum concentrations released from the main source discharging into the Jonathan Run stream, as shown in Table 9, were 105 mg/L for the period 1999 -2003, and decreased to 48 mg/L for the period 2003-2008, reaching an apparent steady state, as shown in Figure 7. The field pH of this main discharge, as reported on Table 9, and shown graphically on Figure 8, averaged 4.1 for the first period, and 3.5 for the second period.

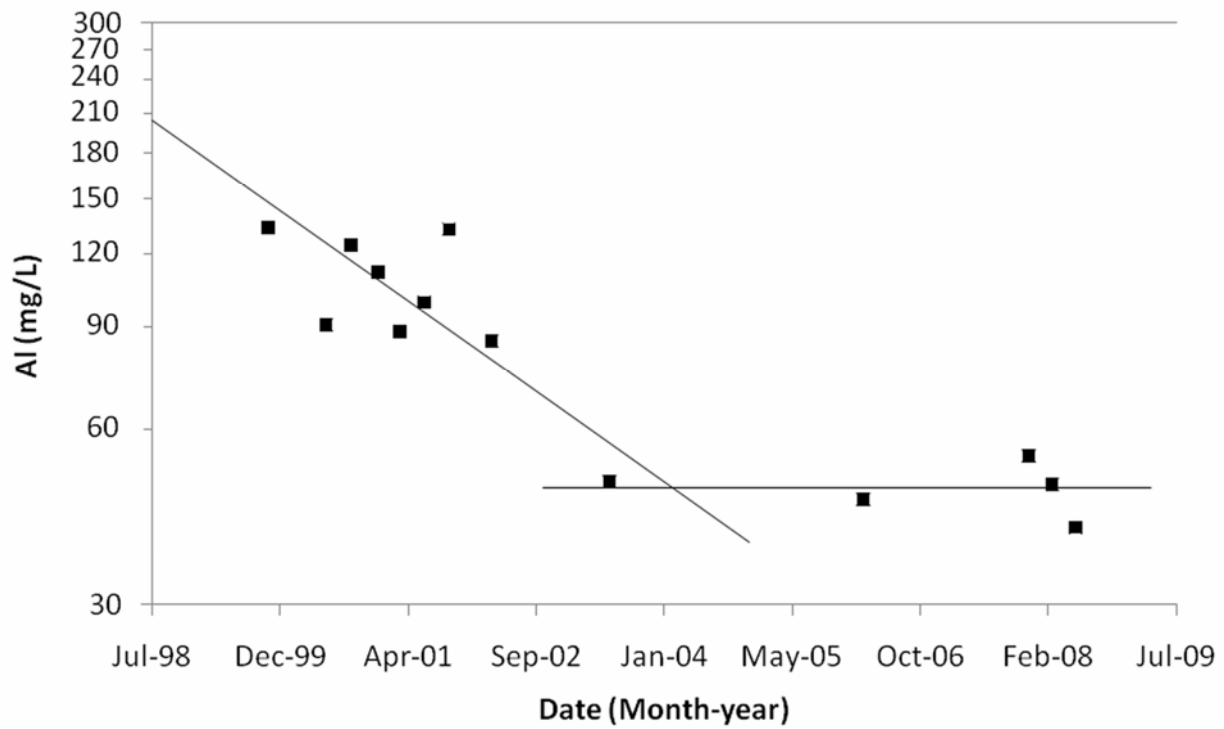


Figure 7. Levels of aluminum released vs. time from the main subsurface seep discharging into the Jonathan Run stream at Centre County, PA (1999-2008)

Table 9. Averaged quarterly values of field pH and Al from the main subsurface seep discharging into the Jonathan Run stream at Centre County, PA (1999-2008)

	Field pH	pH Sd. Dev.	Al (mg/L)	Al Sd. Dev.
Period 1999-2003 n = 9	4.1	0.4	105	28.9
Period 2003-2008 n=4	3.5	0.3	48	6.4

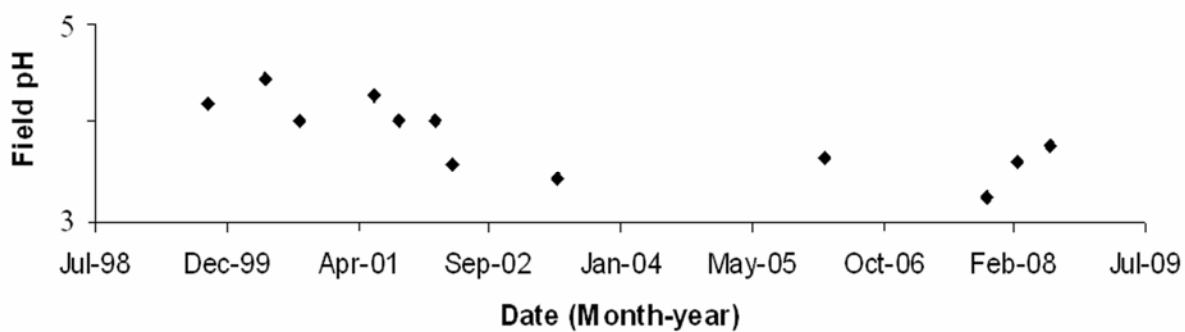


Figure 8. Field pH from the main subsurface seep discharging into the Jonathan Run stream at Centre County, PA (1999-2008)

Batch laboratory leaching of smectite clays

The batch laboratory leaching experiments were conducted to quantify the sorption of ferrous iron and the release of Al from smectite clays at acidic pH values commonly found in AMD/ARD.

The concentration of aluminum leached from smectite in batch reactors approached steady-state values after around 1,000 hours (<2 months) of leaching time. The theoretical initial chemical composition in the smectite-sulfuric acid mixture was <1 mg/L of Al, 5 mg/L of total Fe and 442 mg/L of Na at pH 3.1 as shown in Table 5. The initial iron levels of around 5 mg/L, detected in the smectite-sulfuric acid mixture, represent iron impurities released from the structure of smectite at the initial pH 3 environment. The total iron (ferrous and ferric iron) levels in this mixture and throughout the experiment remained stable (around 5 mg/L). The pH increased over time as shown in Figure 9, from an initial value of around 3 to a steady-state value of around 3.8. The sodium concentrations increased from an initial concentration of over 440 mg/L to a steady-state value of around 500 mg/L (Figure 9). The steady-state aluminum level in this smectite-sulfuric acid mixture at initial pH ~3 was below the practical quantitation limit of 1 mg/L (0.74 $\mu\text{mol/g}$).

The theoretical initial chemical composition in the smectite and ARD mixture was <1 mg/L of Al, 516 mg/L of Fe^{2+} and 442 mg/L of Na at pH 3.1 as shown in Table 5. Aluminum in the smectite-ARD mixture was initially released quickly [and its concentration increased] from <0.74 $\mu\text{mol/g}$ to around 1.9 $\mu\text{mol/g}$, concomitant with a sharp decrease of ferrous iron concentrations, from around 500 mg/L to around 250 mg/L, within the first 80 hours. This is shown on Figures 10-11, respectively. Likewise, there was an initial and sharp increase of

sodium from over 440 mg/L to over 560 mg/L. This first stage of fast release of cations suggest that exchange reactions involving ferrous iron in ARD and sodium and aluminum on the surface of the clay took place within the first hours within the reactor. The initial rapid release of aluminum was followed by a second stage of slower release of aluminum at a relatively constant rate, in the presence of excess clay, giving the appearance of a zero order reaction, from around 1.9 to 2.3 $\mu\text{mol/g}$ (approaching steady-state). During this second stage, the iron and sodium concentrations in the smectite-ARD mixture were stable, suggesting that slow clay dissolution processes dominated the long-term release of aluminum.

Once steady-states were attained in these mixtures, the aluminum released to a mixture of smectite – ARD containing initial ferrous iron concentrations of about 500 mg/L was at least 3 times higher than the aluminum released to a smectite – sulfuric acid mixture at the same initial pH value of around 3. This illustrates that aqueous ferrous iron exacerbates the leaching of aluminum from smectites.

The dissolution reaction rates of clays are generally slow, in contrast to the exchange reaction rates, which are typically fast (Li et al., 2006). The slowest rate of release of aluminum from a mixture of smectite and synthetic ARD seems to be consistent with the second stage (2003-2008) of aluminum released from the main subsurface seep discharging into the Jonathan Run stream at Centre County, PA, as illustrated in Figure 7. This second state of aluminum released from this main subsurface seep and discharging into the Jonathan Run stream appear to follow a zero order rate reaching eventually an apparent steady-state at about 48 mg/L in the field. Likewise, the rapid release of aluminum concomitant with a sharp decrease of ferrous concentrations in a mixture of smectite and synthetic ARD (within 80 hours as shown in Figures 10-11), appears to be consistent with the first stage (1999-2003) of aluminum released from the

main subsurface seep discharging into the Jonathan Run stream at Centre County, PA, as shown in Figure 7.

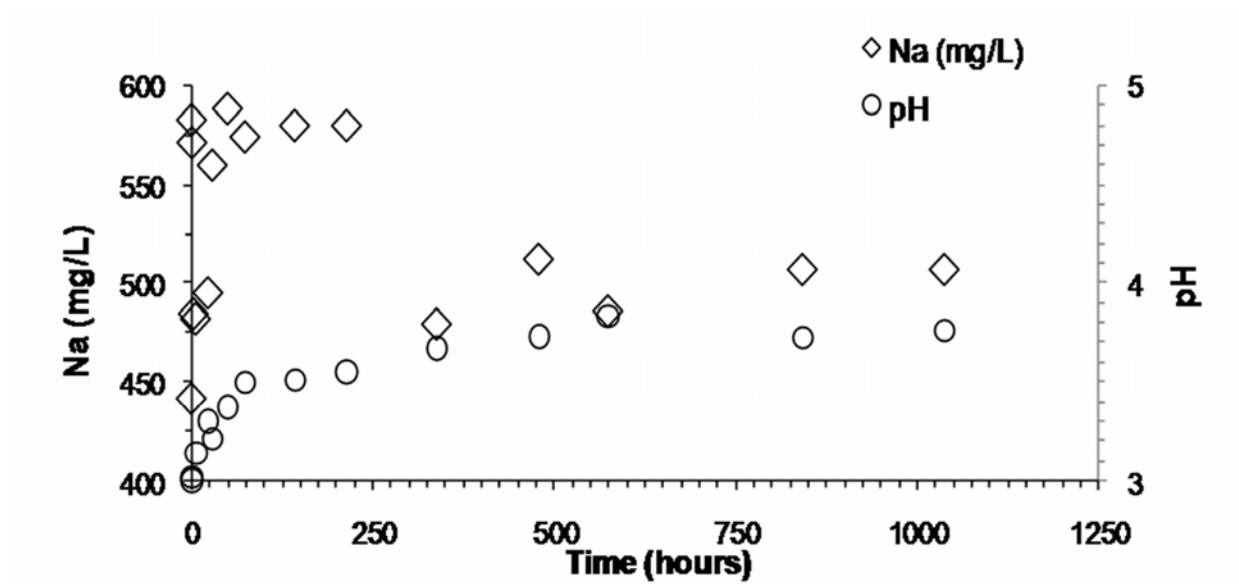


Figure 9. Levels of pH and Na vs. time in a mixture of smectite and sulfuric acid solution

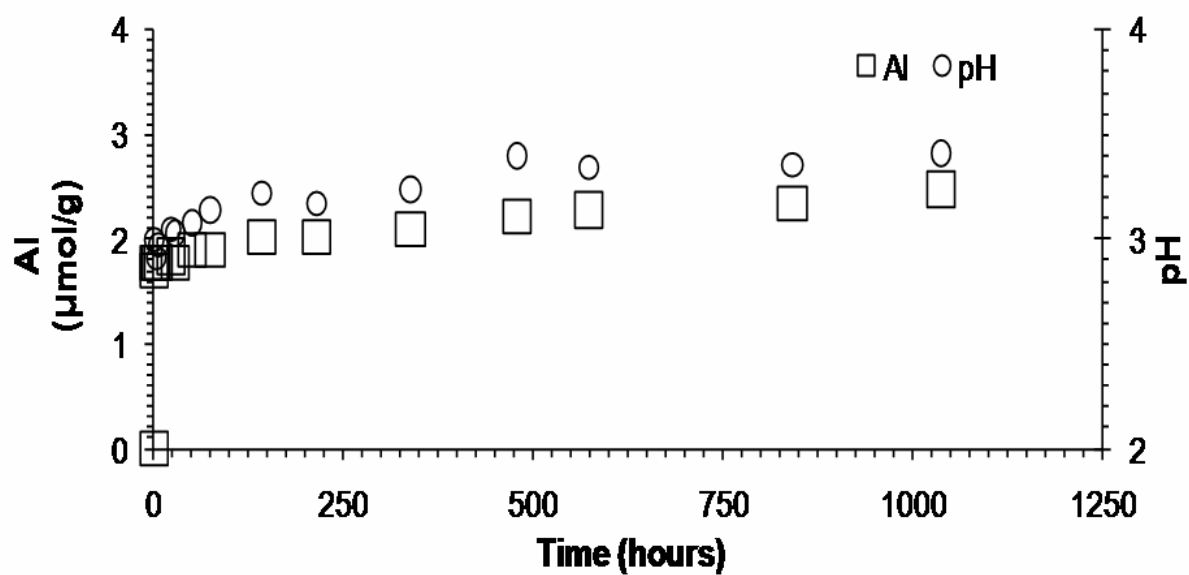


Figure 10. Levels of Al and pH vs. time in a mixture of smectite and conventional
ARD

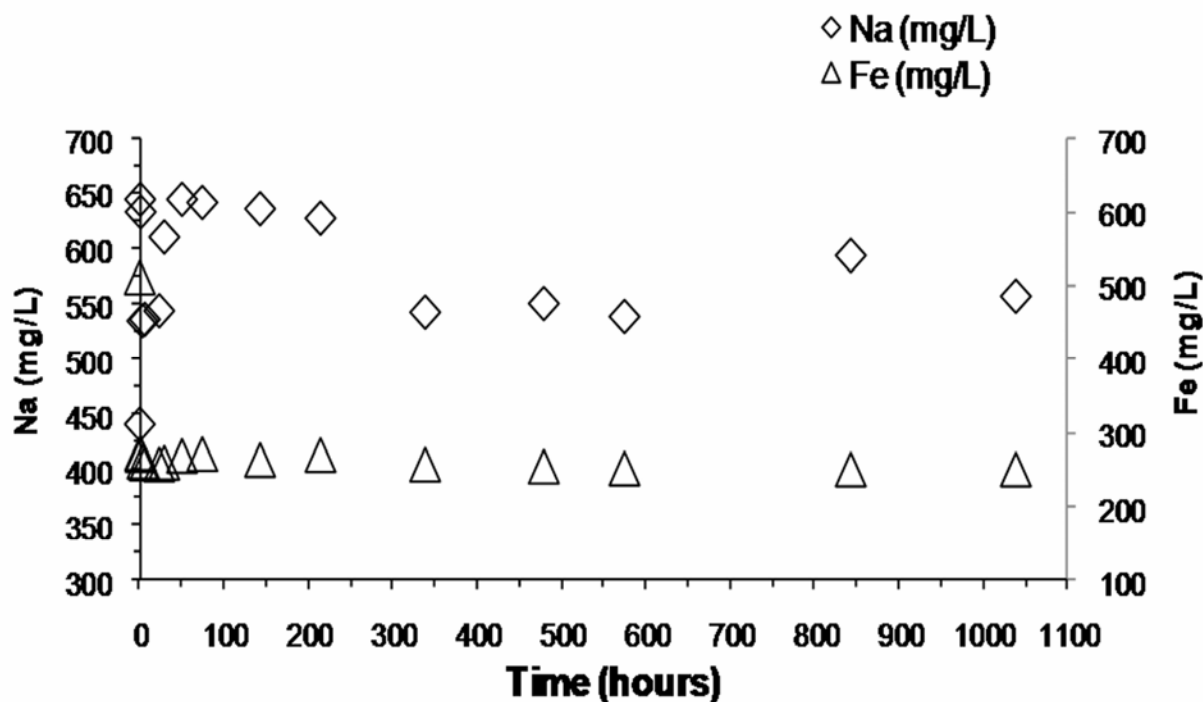


Figure 11. Levels of Fe and Na in a mixture of smectite and conventional ARD

From a comparison of the evolution of aluminum released from these batch experiments and the early stage in the historical data (1999-2003) from ARD discharging from the I-80 culvert into the Jonathan Run stream (as shown in Figure 7), it appears that the site over this time period was still in the stage of evolution of aluminum that is dominated by exchange processes, involving high-CEC and acid unstable Al-bearing clays, such as smectites. This first stage was followed by a second stage that suggests aluminum release dominated by longer term dissolution processes. These results are consistent with the observed low iron concentrations in ARD from this Centre County pyritic sandstone and shale fill at the Jonathan Run site.

The aluminum released from the surface of the smectite clay due to ion-exchange processes took place quickly within the first 80 hours of leaching in the laboratory at the chemical ratios employed. These results suggest that the effect of other cations in ARD, such as potassium and sodium, on the release of aluminum from the surface of other common families of clays found in ARD locations can be further investigated by conducting experiments of duration shorter than the time frames for this phenomena as found in the field.

4.1.2 Short-term leaching of smectites, kaolinites & field clay soil with brackish acid drainages

The release of aluminum from the surface of acid smectite and kaolinite clays and field clay soil collected at the Jonathan Run site was investigated. On June 3rd, 2010, soil sampling was conducted at the Jonathan Run site by researchers from the Civil and Environmental Department (CEE) of University of Pittsburgh. Clay soil samples were collected downstream of the main source of ARD at the Jonathan Run site. The location of the sampling site is shown in Figure 6. The water contained in this clay soil collected at the northern side of Interstate 80 was analyzed for Al, Fe, K, Na and SiO₂. The pore water composition of the clay soil collected is shown in Table 10. The high concentrations of aluminum and low pH values in the pore water of this clay soil suggest that the H/Al composition of the adsorption complex of this clays soil represents an important percentage of its CEC, far beyond 20%, and confirms it as an acid clay soil.

The laboratory leaching batch experiments involved leaching of these acid clays with synthetic brackish and conventional (non-brackish) ARD as well as sulfuric leaching solutions. The exchange reactions between ferrous iron and exchangeable aluminum on the surface of these

clays were considered as a possible explanation for the observed low iron concentrations in some ARDs. The influence of brackish ARD groundwater with Na and K salts on the observed release of aluminum from these clays was investigated as well. The results from these batch experiments suggest that synthetic brackish ARD enhances the release of aluminum from the surface of these clays, compared to synthetic acid (sulfuric) only and conventional (non-brackish) ARD (Vazquez et al., 2010).

Table 10. The pore water composition surrounding field clay soil from the Jonathan Run site*

pH	Total Al (mg/L)	Total SiO₂ (mg/L)	Total Fe (mg/L)	Total K (mg/L)	Total Na (mg/L)
3.1	25	25	<2	2	4

*Note: this clay-soil was collected in the summer of 2010, and from a location where it was not directly impacted by any road salts that may have been released from the deicing of I-80. This would explain the low sodium content of pore waters.

The experimental data obtained for kaolinite, H/Al-bentonite, and clay soil from the Jonathan Run site at Centre County, PA, at a wt/wt soil to solution ratio of 1:10 (10% wt/wt), are summarized in Table 11.

The Al levels shown for the Centre County clay soils in this table were corrected subtracting the Al initially present in the pore water of the clay sample to the results of the Al analysis. For this purpose, the volume of pore water per gram of dried clay soil sample (0.78 ml/g clay) was previously determined. This factor was then used with the concentration of Al (25 mg/L) found in the pore water of Centre County clay soil (Table 10) to determine the Al initially present in the pore water. Thus, the Al levels in Table 11 represent those actually leached from the Centre County clay soil due to the different leaching solutions. The decrease of sodium after 67 hours of leaching remained below 5% of the initial concentrations of sodium in brackish ARD (ARD 2) (Table 11), suggesting minor sorption of sodium onto kaolinite and clay soil from the Jonathan Run site at Centre County, PA. Figure 12 and Table 12, respectively, show the release of aluminum and cation sorption per unit mass of each of these clays. The data indicate that brackish waters in an ARD environment (ARD 2) enhance the release of aluminum from these clays, compared to acidic (sulfuric acid) or non-brackish ARD environments (ARD 1).

Table 11. Experimental results after 67 hours of leaching of kaolinite, Centre County clay soil and H/Al-bentonite with different leaching solutions

	Leaching solutions	Concentrations	pH± stdev ⁵	^{*,4} Total Al± stdev ⁵	[*] Fe ²⁺ ± stdev ⁵	[*] K ⁺ ± stdev ⁵	[*] Na ⁺ ± stdev ⁵
Kaolinite	Sulfuric acid	Initial	2.7±0.0	¹ <1	² <2	² <2	³ <5
		Final	3.3±0.1	¹ <1	² <2	5.0±0.5	5.5±1.3
	ARD 1	Initial	3.2±0.0	¹ <1	673±0	² <2	³ <5
		Final	3.4±0.0	2.3±0.1	620±2	6.8±0.1	5.7±0.3
	ARD 2	Initial	3.4±0.0	¹ <1	621±14	529±5	992±25
		Final	3.7±0.0	3.2±0.1	596±0	507±7	978±4
Centre County clay soil	Sulfuric acid	Initial	2.7±0.1	¹ <1	² <2	² <2	⁶ <0.2
		Final	3.1±0.1	¹ <1	² <2	² <2	1±0.3
	ARD 1	Initial	3.2±0.1	¹ <1	547±1.4	² <2	⁶ <0.2
		Final	3.4±0.1	14.1±0.5	464±2.8	² <2	¹ <1
	ARD 2	Initial	3.3±0.1	¹ <1	518±8.5	511±9.9	949±4.2
		Final	3.6±0.1	18.2±0.7	458±2.8	486±14.1	921±4.2
H/Al-bentonite	Sulfuric acid	Initial	2.6±0.0	¹ <1	² <2	² <2	¹ <1
		Final	2.5±0.0	¹ <1	² <2	4.8±1.4	6.2±0.3
	ARD 1	Initial	3.1±0.0	¹ <1	506±19	² <2	¹ <1
		Final	2.5±0.0	26.5±1.0	186±0.0	4.0±0.3	7.6±0.0
	ARD 2	Initial	3.3±0.0	¹ <1	540±14	568±2.8	821±12.7
		Final	2.5±0.0	48.1±1.3	252±6	421±18	721±1.4

*All concentrations in mg/L. ¹Below practical quantitation limit (PQL) of 1 mg/L. ²Below PQL of 2 mg/L. ³Below PQL of 5 mg/L. ⁴Determination of aluminum with non digested samples. ⁵stdev=standard deviation. ⁶Below PQL of 0.2 mg/L.

Sorption/exchange of cations

From Figure 12 and Table 12, it can be seen that the release of aluminum and sorption of cations on these clays, expressed as $\mu\text{eq/g}$ of clay, are higher for H/Al-bentonite than for kaolinite clays. These results are consistent with the reported higher chemical degradation of H/Al-bentonites (smectite group), relative to other clays, under acidic conditions (Galan et al., 1999) and the higher cation exchange capacity of the H/Al-bentonites (smectite group) compared to the kaolinites (Angove and Johnson, 1997; Chukwudi, 2008; Giese et al., 2002).

Sorption of ferrous iron cations per gram of selected clays varied from around 8% (kaolinite) to a maximum of 63% (H/Al-bentonite) of the initial ferrous iron in the synthetic ARD solutions, as inferred from Table 12. Sorption of potassium cations per gram of selected clays varied from 4% (kaolinite) to 26% (H/Al-bentonite) of the initial potassium in the brackish ARD 2. Sorption of sodium cations per gram of selected clays varied from near 0% (kaolinite and field-collected clay soil) to 12% (H/Al-bentonite) of the initial sodium in ARD 2. It therefore appears that sodium had a minor influence on the release of Al from kaolinite. On the other hand, sorption of ferrous iron and potassium cations in addition to the sodium present on the H/Al-bentonite suggests that all of these cations (Fe^{2+} , K^{+} and Na^{+}) can enhance the release of aluminum from H/Al-bentonite. The magnitude of cation sorption on clay soil from the Jonathan Run site at Centre County, PA was between that for kaolinite clays (Na sorption was negligible) and H/Al-bentonite, as shown in Table 12.

The aluminum released per gram of Centre County clay soil, 15.7 $\mu\text{eq/g}$, was within the range of aluminum released from kaolinite and H/Al-bentonite clays, 2.6 and 29.4 $\mu\text{eq/g}$, respectively, when these clays were leached with synthetic non-brackish ARD 1 (Figure 12). Similarly, when the clays were leached with the brackish ARD 2 (Figure 12), the aluminum released per gram of Centre County clay soil of 20.2 $\mu\text{eq/g}$, was within the range of aluminum released from kaolinite and H/Al-bentonite clays of 3.6 and 53.4 $\mu\text{eq/g}$, respectively.

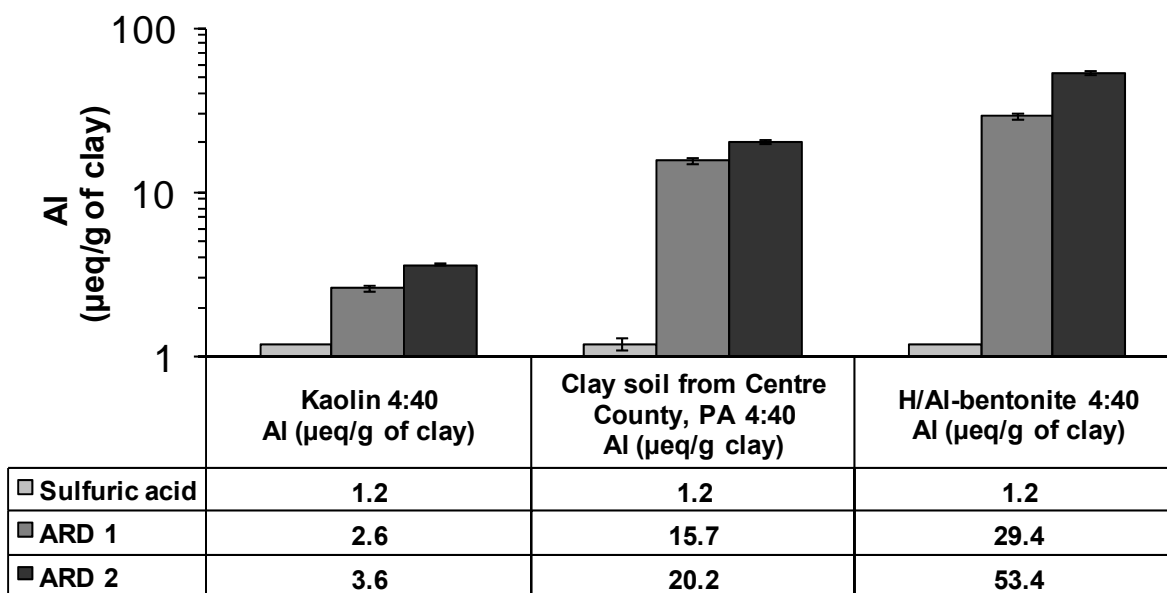


Figure 12. The aluminum released per gram of kaolin, Centre County clay soil and H/Al-bentonite after 67 hours of leaching with different leaching solutions

Table 12. Cation sorption into kaolinite, clay soil from Centre County, PA and H/Al-bentonite after 67 hours of leaching with different leaching solutions

	Leaching solutions	$\mu\text{eq/g}$					
		Sorbed H^+	Sorbed Fe^{2+}	Sorbed K^+	Sorbed Na^+	Overall cation sorption ($\text{H}^+ + \text{Fe}^{2+} + \text{K}^+ + \text{Na}^+$)	Released Al
Kaolinite	Sulfuric acid	14.9	N.D.	N.D.	N.D.	14.9	<1.2
	ARD 1	2.3	19	N.D.	N.D.	21.3	2.6
	ARD 2	2.0	N.D.	5.6	N.D.	7.6	3.6
Centre County clay soil	Sulfuric acid	12.0	N.D.	N.D.	N.D.	12.0	<1.2
	ARD 1	2.3	29.7	N.D.	N.D.	32	15.7
	ARD 2	2.5	21.5	6.4	N.D.	30.4	20.2
H/Al-bentonite	Sulfuric acid	N.D.	N.D.	N.D.	N.D.	N.D.	<1.2
	ARD 1	N.D.	115	N.D.	N.D.	115	29.4
	ARD 2	N.D.	103	37.6	43.5	184.1	53.4

N.D. - No Detected or minor (cation concentration decrease within 5% of the initial cation concentration in the leaching solution (ARD 1 or ARD 2).

4.1.3 Summary from phase 1 leaching (preliminary studies)

Based on the results from these experiments the following conclusions are drawn:

1. The steady state aluminum concentration (2.3 $\mu\text{mol/g}$) in a mixture of smectite and synthetic ARD is at least 3 times higher than the aluminum concentration in a mixture of smectite and sulfuric acid <0.74 $\mu\text{mol/g}$ for the same initial pH ~ 3 .
2. An early release of aluminum (first 80 hours of leaching) from smectite clays leached with synthetic ARD from <0.74 $\mu\text{mol/g}$ to around 1.9 $\mu\text{mol/g}$, is dominated by exchange reactions involving ferrous iron and H^+ .
3. Long term release of aluminum from smectite clays leached with synthetic ARD appears to be dominated by smectite dissolution processes, resulting in aluminum concentrations up to 2.3 $\mu\text{mol/g}$ once steady state is approached.
4. The release of aluminum from the surface of kaolinite and H/Al-bentonite (smectite group) clays is enhanced by potassium (K) salts (KCl) in synthetic ARD.
5. Sodium (Na) salts (NaCl) in synthetic ARD enhance the release of aluminum from the surface of H/Al-bentonite clays but these salts have a minor effect on the release of aluminum from the surface of kaolinite.

4.2 PHASE 2 LEACHING

Preliminary research (Phase 1 above) has showed that in general cation sorption and aluminum released per gram of clays leached with synthetic ARD solutions with different concentrations of ferrous iron, potassium and sodium salts at pH of 3 were significantly higher for smectite than for kaolinite clays. The phase 2 of leaching experiments used a broader range of concentrations of ferrous iron (0-1000 mg/L), potassium (0-50000) and sodium (0-50000) and pH (2-3). The phase 2 experiments further investigated the relative effect of the concentrations of these metals (Fe^{2+} , K^{+} and Na^{+}) on the release of aluminum from clays. The analysis of silicate released from smectite clays was also determined in phase 2 to further clarify the mechanisms dominating the long-term release of aluminum from clays. This second phase of experiments also focused on the release of aluminum from smectite clays which are widespread. Furthermore, smectite clays as shown in phase 1 have a higher potential for the generation of AMD/ARD containing high concentrations of aluminum.

This work will offer insight into some issues of possible significance. The effect of the high concentrations of sodium and potassium salts in AMD/ARD on the release of aluminum from clays may be noteworthy. Possible outcomes include that highway deicing salts in road runoff could aggravate the leaching of aluminum from pyritic rocks used as a fill or exposed in road cut. Furthermore, AMD/ARD used as a source of fracturing fluid to boost natural gas production, such as the Marcellus shale unit, could influence the release of aluminum. A better understanding of the occurrence of high concentrations of aluminum in AMD/ARD will assist

others to consider alternative remediation strategies in those locations where the in-situ generation of high concentration of aluminum discharges occurs.

Aluminum typically is observed in AMD/ARD when the local bedrock and soil contain aluminum-bearing minerals, such as clays, and other aluminosilicate mineral phases (Rozalen et al., 2009). Smectite clays, $M_x[Mg_{0.66}Al_{3.34}][Si_8]O_{20}(OH)_4(H_2O)_n$ -where x commonly represents 0.33 exchangeable divalent cations (generally Ca) or 0.66 monovalent cations (generally Na or K) (Metz et al., 2005), are the most common phyllosilicates in soils and sediments (Sondi et al., 2008). The prevalence of smectite and other aluminum bearing minerals in soils in the Appalachian mining region of the U.S. increases the potential for the generation of AMD/ARD with high concentrations of aluminum. The overall experimental data obtained after long-term leaching of smectite clays with different leaching solutions at pH of 2 and 3 is shown in Appendices A-B. The results and discussion of the data in this section focused in the effect of the most significant cations in these leaching solutions, as shown in Table 12; ferrous iron, potassium and sodium, on the release of aluminum from smectite clays.

4.2.1 Aluminum

The aluminum levels released overtime from the smectite clay to the different leaching solutions at initial pH values of around 2 and 3 are shown in Figures 13-14. The levels of aluminum released to the sulfuric acid leaching solution at initial pH of 2 were detectable throughout the leaching experiment. The steady-state aluminum levels in this sulfuric acid leaching solutions at pH of 2 reached values of around 1100 $\mu\text{g/g}$ clay as shown in Table 13.

The leaching solutions termed as AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000 contained initially different high concentrations of ferrous iron, potassium and sodium (Table 8). The steady-state aluminum levels released to these leaching solutions (AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000) were significantly higher than those in sulfuric acid leaching solutions at the same initial pH of 2 (Table 13). The steady-state aluminum levels in these “AMD” leaching solutions varied from around 2000 $\mu\text{gAl/g}$ clay (AMD1_500 and AMD2_50000) to around 2600 $\mu\text{gAl/g}$ clay (AMD1_1000 and AMD2_500) as shown in Figure 13 and Table 13. These data suggest that Fe^{2+} , K^+ and Na^+ in AMD/ARD at pH of 2 enhance the release of aluminum from smectite clays.

The leaching solution termed as AMD1_1000 contained initially ferrous iron concentrations of around 1000 mg/L. Likewise, the leaching solution termed as AMD1_500 contained initially ferrous iron concentrations of around 500 mg/L (Table 8). The steady-state Al level in AMD1_1000 (2600 $\mu\text{gAl/g}$ clay) was higher than that in AMD1_500 (~2000 $\mu\text{gAl/g}$ clay) at pH 2 (Table 13). These data suggest that higher initial concentrations of ferrous iron in AMD/ARD at pH 2 resulted in higher levels of aluminum leached from the smectite clay at steady-state.

The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L (Table 8). The steady-state Al level in AMD2_500 (~2600 $\mu\text{gAl/g}$ clay) was higher than that in AMD1_500 (~2000 $\mu\text{gAl/g}$ clay) at pH 2 (Table 13). These data suggest that high initial concentrations of potassium and sodium in AMD/ARD at pH 2 enhance the levels of aluminum leached from smectite clays. The steady state Al level in AMD2_500 was close to that in AMD1_1000 (~2600 $\mu\text{gAl/g}$ clay) at

pH 2 (Table 13). Thus, the affinity of ferrous iron in AMD/ARD at pH 2 for the smectite surface is significant as compared to the affinity of potassium and sodium.

The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). Thus, the initial overall concentration of cations (Fe^{2+} , K^+ and Na^+) in AMD2_50000 (3167 $\mu\text{eq/L}$) is significantly higher than that in AMD2_500 (66 $\mu\text{eq/L}$) or AMD1_1000 (41 $\mu\text{eq/L}$) at pH 2 (figures derived from Table 8). Moreover, the steady state Al level in AMD2_50000 (~2000 $\mu\text{gAl/g clay}$) was lower than that in AMD1_1000 and AMD2_500 (~2600 $\mu\text{gAl/g clay}$) at pH 2 (Table 13). These data suggest the extreme overall initial level of cations (Fe^{2+} , K^+ and Na^+) in AMD2_50000 (3167 $\mu\text{eq/L}$) at pH 2 may have promoted the precipitation of Al solid phases. The precipitation of these Al solid phases would lead to lower steady state Al levels in AMD2_50000 as compared to those in AMD1_500, AMD1_1000 and AMD2_500 at pH 2.

The Al levels released to the control leaching solution (deionized water (D.W.) leaching solution) were non-detectable throughout the leaching experiments. The Al levels released overtime to the sulfuric acid leaching solution at initial pH of 3 were non-detectable throughout the leaching experiment (<1mg/L or 80 $\mu\text{gAl/g clay}$ within experimental conditions). Thus, the steady-state aluminum level in the sulfuric acid leaching solution at pH of 2 (1100 $\mu\text{gAl/g clay}$) (Table 13) was much higher than that in the same leaching solution at pH 3 (<80 $\mu\text{gAl/g clay}$) (Table 14). These data show that low pH values in AMD/ARD favor the release of Al from smectite clays. Thus, pH is a chief factor in the release of Al from smectite clays.

The leaching solutions termed as AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000 contained initially different high concentrations of ferrous iron, potassium and

sodium (Table 8). The steady-state aluminum levels released to these leaching solutions (AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000) were significantly higher than those in sulfuric acid leaching solutions at the same initial pH of 3 (Table 14). The steady-state aluminum levels in these leaching solutions varied from around 900 $\mu\text{gAl/g}$ clay (AMD1_500) to around 2000 $\mu\text{gAl/g}$ clay (AMD2_50000) as shown in Figure 14 and Table 14. These data suggest that these cations (Fe^{2+} , K^{+} and Na^{+}) in AMD/ARD at pH of 3 enhance the release of aluminum from smectite clays.

The leaching solution termed as AMD1_1000 contained initially ferrous iron concentrations of around 1000 mg/L. Likewise, the leaching solution termed as AMD1_500 contained initially ferrous iron concentrations of around 500 mg/L (Table 8). The steady-state Al level in AMD1_1000 (~ 1700 $\mu\text{gAl/g}$ clay) was higher than that in AMD1_500 (~ 900 $\mu\text{gAl/g}$ clay) at pH 3 (Table 14). These data suggest that higher initial concentrations of ferrous iron in AMD/ARD at pH 3 result in higher levels of aluminum leached from the smectite clay at steady-state.

The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L (Table 8). The steady-state Al level in AMD2_500 (~ 1300 $\mu\text{gAl/g}$ clay) was higher than that in AMD1_500 (~ 900 $\mu\text{gAl/g}$ clay) at pH 3 (Table 14). These data suggest that high initial concentrations of potassium and sodium in AMD/ARD at pH 3 result in higher levels of aluminum leached from smectite clays at steady-state. The steady state Al level in AMD2_500 (~ 1400 $\mu\text{gAl/g}$ clay) was lower to that in AMD1_1000 (~ 1700 $\mu\text{gAl/g}$ clay) at pH 3 (Table 14). Thus, the affinity of ferrous iron in

AMD/ARD at pH 3 for the smectite surface is significant as compared to the affinity of potassium and sodium.

The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). Thus, the initial overall concentration of cations (Fe^{2+} , K^+ and Na^+) in AMD2_50000 (3268 $\mu\text{eq/L}$) is significantly higher than that in AMD2_500 (68 $\mu\text{eq/L}$) or AMD1_1000 (41 $\mu\text{eq/L}$) at pH 3 (figures derived from Table 8). The steady state Al level in AMD2_50000 (~2000 $\mu\text{g/g}$) was higher than that in AMD1_1000 and AMD2_500 (~1700 $\mu\text{g/g}$ of Al) at pH 3 (Table 14). The steady state Al level in AMD2_50000 at pH 2 was similar than that in AMD2_50000 at pH 3 (~2000 $\mu\text{g/g}$) (Tables 13-14). The data suggest that extreme concentrations of potassium (~50000 mg/L) and sodium (~50000 mg/L) in AMD/ARD appear to mask the key effect of pH on the release of Al from smectite clays at pH of 2-3.

The steady-state Al level in sulfuric acid solutions at initial pH of 2 (~1000 $\mu\text{gAl/g}$ clay) (Table 13) was higher than that in AMD1_500 at initial pH of 3 (~ 900 $\mu\text{gAl/g}$ clay) (Table 14). These results are consistent with the pH being a key factor in the release of Al from smectite clays.

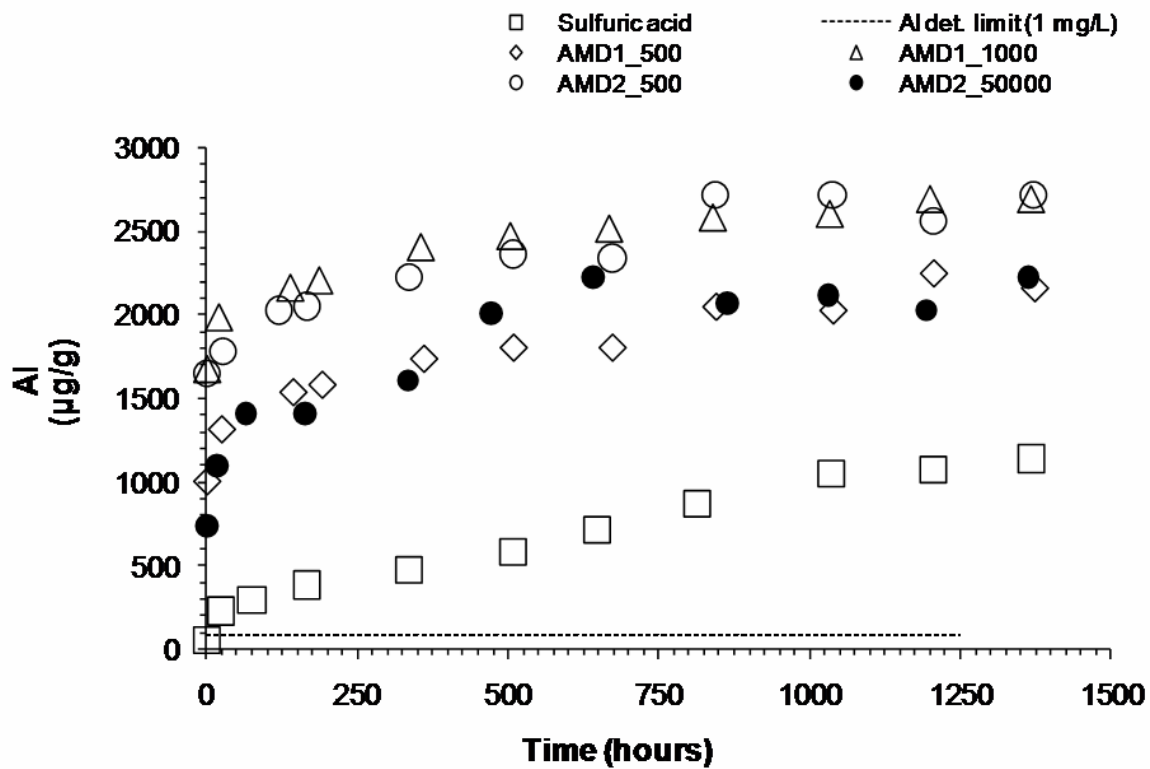


Figure 13. Levels of Al vs. time in leaching solutions at pH 2

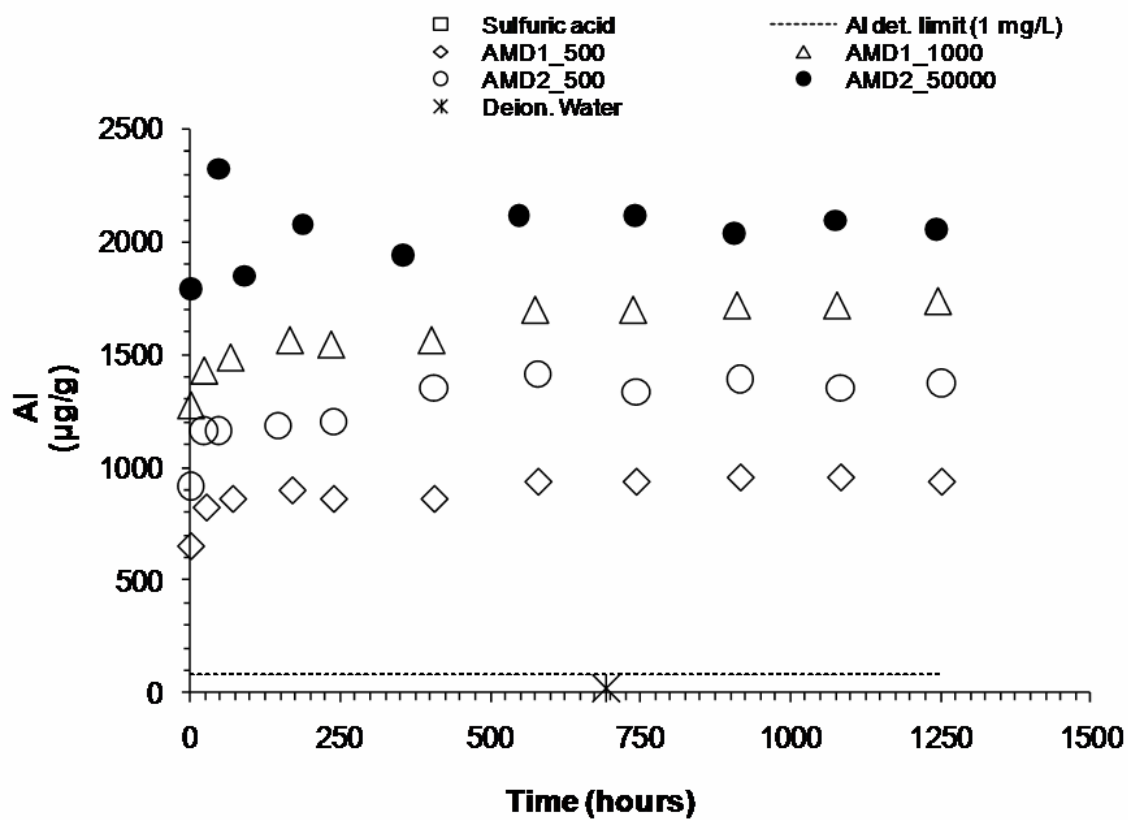


Figure 14. Levels of Al vs. time in leaching solutions at pH 3

Table 13. The steady-state pH and aluminum levels released from smectite clays to the different leaching solutions at initial pH 2

Leaching solution	pH	¹ Al (µg/g)
D.W.	3.2	² <80
Sulfuric acid	2.0	1088
AMD1_500	2.0	2144
AMD1_1000	2.0	2648
AMD2_500	2.0	2664
AMD2_50000	2.1	2112

¹ Steady-state Al levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest Al levels, respectively. ² Practical quantitation limit (PQL) was 1 mg/L (=80 µg/g) for Al.

Table 14. The steady-state pH and aluminum levels released from smectite clays to the different leaching solutions at initial pH 3

Leaching solution	pH	¹ Al (µg/g)
Sulfuric acid	2.9	² <80
AMD1_500	2.6	944
AMD1_1000	2.6	1712
AMD2_500	2.7	1376
AMD2_50000	2.8	2088

¹ Steady-state Al levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest Al levels, respectively. ² Practical quantitation limit (PQL) was 1 mg/L (=80 µg/g) for Al.

In summary, the data in this subsection show that low pH values in leaching solutions favor the release of Al from smectite clays. Moreover, high levels of Fe^{2+} , K^+ and Na^+ in leaching solutions at pH 2 and 3 enhance the release of Al from smectite clays. The higher the initial levels of Fe^{2+} in these leaching solutions, the higher the levels of Al leached from the smectite clay to the leaching solutions. The presence of K^+ and Na^+ in these leaching solutions also enhances the release of Al from the smectite to the leaching solutions as compared to the case of leaching solutions with no initial K^+ and Na^+ . The affinity of Fe^{2+} in these leaching solutions for the smectite surface is significant as compared to the affinity of K^+ and Na^+ .

The steady state Al levels in leaching solutions containing initially extreme levels of K^+ (~50000 mg/L) and Na^+ (~50000 mg/L) at pH 2 and 3 were similar. The extreme K^+ and Na^+ levels in these leaching solutions appear to mask the key effect of pH on the release of Al from smectite clays. This is consistent with the precipitation of secondary solid phases containing Al. This effect appears to lead to lower than expected steady-state levels of Al in these leaching solutions as compared to those found in leaching solutions initially containing lower Fe^{2+} , K^+ and Na^+ levels at pH 2.

4.2.2 Silica

The levels of silica leached from clays are markers or indicators of the extent of dissolution of clays by leaching media. The silica levels released overtime from the smectite clay to different leaching solutions at initial pH values of around 2 and 3 are shown in Figures 15-16. The steady-state silica level in the sulfuric acid leaching solution at pH of 2 reached values of around 9400 $\mu\text{g SiO}_2/\text{g clay}$ as shown in Figure 15 and Table 15. The leaching solutions termed as AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000 contained initially different high concentrations of ferrous iron, potassium and sodium (Table 8). The steady-state silica levels released to these leaching solutions (AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000) were significantly lower than those in sulfuric acid leaching solutions at the same initial pH of 2. The steady-state silica levels in these leaching solutions varied from around 3900 $\mu\text{g SiO}_2/\text{g clay}$ (AMD2_50000) to around 7800 $\mu\text{g SiO}_2/\text{g clay}$ (AMD1_500) as shown in Figure 15 and Table 15. Overall, these data suggest that the absence of high initial levels of cations (Fe^{2+} , K^+ and Na^+) in leaching solutions at pH 2 favors the presence of high levels of silica at steady-state.

The leaching solution termed as AMD1_1000 contained initially ferrous iron concentrations of around 1000 mg/L. Likewise, the leaching solution termed as AMD1_500 contained initially ferrous iron concentrations of around 500 mg/L (Table 8). The steady-state silica level in AMD1_1000 (~6900 $\mu\text{g SiO}_2/\text{g clay}$) was lower than that in AMD1_500 (~7800 $\mu\text{g SiO}_2/\text{g clay}$) at pH 2 (Table 15). The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L. The steady-state silica level in AMD2_500 (~7400 $\mu\text{g SiO}_2/\text{g clay}$) was higher than

that in AMD1_1000 (~6900 $\mu\text{g SiO}_2/\text{g clay}$) at pH 2 (Table 15). Moreover, the steady-state silica level in AMD2_500 (~7400 $\mu\text{g SiO}_2/\text{g clay}$) was lower to that in AMD1_500 (~7800 $\mu\text{g SiO}_2/\text{g clay}$) at pH 2 (Table 15). The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). The steady-state silica level in AMD2_50000 at pH 2 (~3900 $\mu\text{g SiO}_2/\text{g clay}$), was significantly lower than those in the rest of leaching solutions as shown in Table 15. Overall, these data is consistent with higher steady-state levels of silica (SiO_2) in leaching solutions containing initially lower levels of cations (Fe^{2+} , K^+ and Na^+) at pH 2.

The steady-state silica level in the control leaching solution (deionized water (D.W.) leaching solution) (~3800 $\mu\text{g SiO}_2/\text{g clay}$) was higher than that in the sulfuric acid leaching solution (~3400 $\mu\text{g SiO}_2/\text{g clay}$) at pH 3 (Tables 15-16). The leaching solutions termed as AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000 contained initially different high concentrations of ferrous iron, potassium and sodium (Table 8). The steady-state silica levels released to these leaching solutions (AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000) at pH 3 varied from around 3100 $\mu\text{g SiO}_2/\text{g clay}$ (AMD1_1000, AMD2_500 and AMD2_50000) to around 3300 $\mu\text{g SiO}_2/\text{g clay}$ (AMD1_500) as shown in Figure 16 and Table 16. Overall, these data suggest that the absence of high initial levels of cations (Fe^{2+} , K^+ and Na^+) in leaching solutions at pH 3 favors the presence of high levels of silica at steady-state.

The leaching solution termed as AMD1_1000 contained initially ferrous iron concentrations of around 1000 mg/L. Likewise, the leaching solution termed as AMD1_500 contained initially ferrous iron concentrations of around 500 mg/L (Table 8). The steady-state silica level in AMD1_1000 (~3100 $\mu\text{g SiO}_2/\text{g clay}$) was lower than that in AMD1_500 (~3300

$\mu\text{g SiO}_2/\text{g clay}$) at pH 3 (Table 16). The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L (Table 8). The steady-state silica level in AMD2_500 ($\sim 3100 \mu\text{g SiO}_2/\text{g clay}$) was lower than that in AMD1_500 ($\sim 3300 \mu\text{g SiO}_2/\text{g clay}$) at pH 3 (Table 16). The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). The steady-state silica level in AMD2_500 was similar to those in AMD1_1000 and AMD2_50000 ($\sim 3100 \mu\text{g SiO}_2/\text{g clay}$) at pH 3, as shown in Table 16. Overall, these data are consistent with higher steady-state levels of silica (SiO_2) in leaching solutions containing initially lower levels of cations (Fe^{2+} , K^+ and Na^+) at pH 3.

It has been reported that the presence of cations, such as ferrous iron, may enhance the coagulation of clay particles and reduce the dispersion of colloidal particles in solution (Saejiew et al., 2004). The presence of cations, such as Fe^{2+} , K^+ and Na^+ , in our leaching solutions may prevent the presence of SiO_2 colloidal particles in our leaching solutions at steady-state. Thus, the presence of Fe^{2+} , K^+ and Na^+ in these leaching solutions may enhance coagulation of SiO_2 colloidal particles and minimize the presence of silica in these leaching solutions at steady-state.

The release of silica from smectite clays at pH 3 is much lower than at pH 2 as shown in Tables 15-16 and Figures 15-16. Thus, pH is a key factor on the release of silica from the smectite clay and the dissolution of clay in general. The effect of ferrous iron, potassium and sodium in synthetic AMD at initial pH of 2 and 3 on the release of silica from the smectite clay is not as significant as the effect of the pH. However, the effect of the pH in combination with the

ferrous iron, potassium and sodium concentrations in synthetic AMD at initial pH of 2 and 3 on the release of aluminum from smectite clays is significant.

The wt/wt (g/g) percentage of silica (SiO_2) in smectite clay ($\text{Na}_{0.33}\text{Mg}_{0.33}\text{Al}_{1.67}\text{Si}_4\text{O}_{10}(\text{OH})_2$) is approximately 68.5%. The highest steady-state SiO_2 levels ($\sim 10000 \mu\text{g/g}$ clay) released from smectite clay took place when the clay was leached with sulfuric acid at pH 2 (Figure 15 and Table 15). Thus, the percentage of smectite clay dissolved in the worst scenario found in the context of this research (leaching with sulfuric acid at pH 2) can be estimated to be 1.46%. This represents a small number, which explains why there is not much subsidence of the embankment at the Jonathan Run site. This percentage of dissolved smectite clay, however, may lead to a significant aluminum loading to receiving streams.

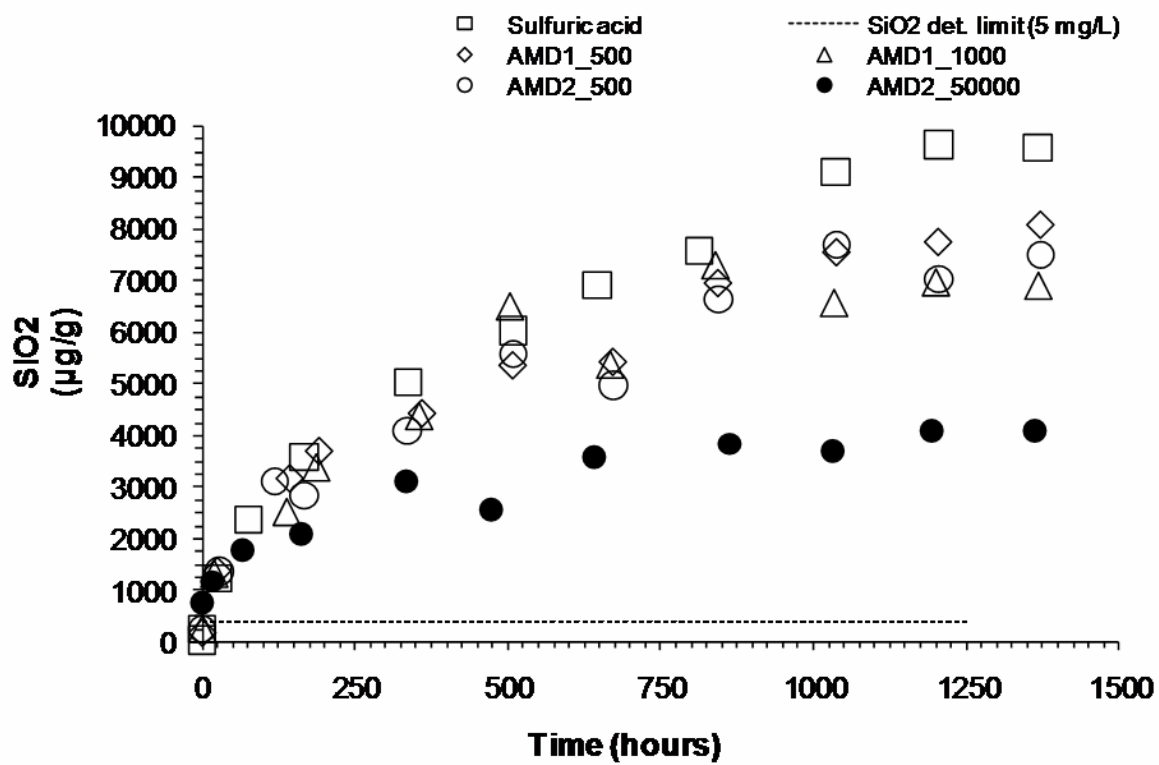


Figure 15. Levels of SiO₂ vs. time in leaching solutions at pH 2

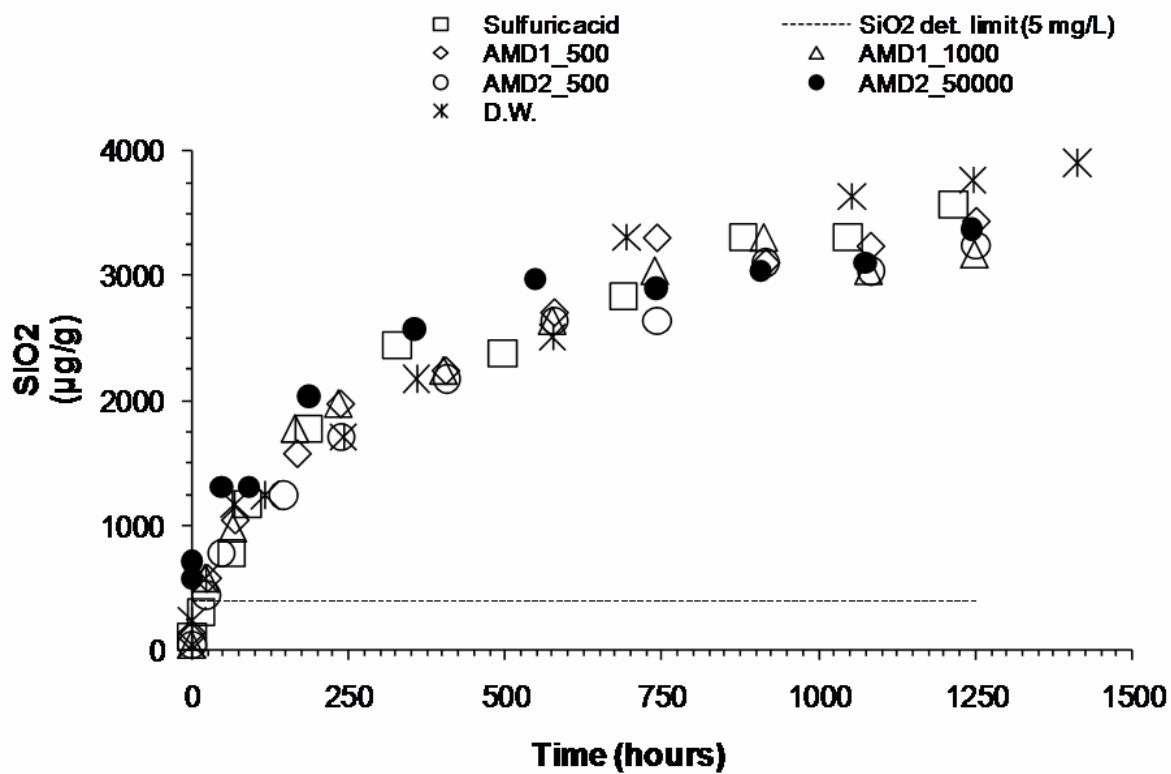


Figure 16. Levels of SiO_2 vs. time in leaching solutions at pH 3

Table 15. The steady-state pH and silica levels released from smectite clays to the different leaching solutions at initial pH 2

Leaching solution	pH	¹SiO₂ (µg/g)
D.W.	3.2	3760
Sulfuric acid	2.0	9440
AMD1_500	2.0	7840
AMD1_1000	2.0	6880
AMD2_500	2.0	7440
AMD2_50000	2.1	3936

¹ Steady-state SiO₂ levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest SiO₂ levels, respectively.

Table 16. The steady-state pH and silica levels released from smectite clays to the different leaching solutions at initial pH 3

Leaching solution	pH	¹SiO₂ (µg/g)
Sulfuric acid	2.9	3360
AMD1_500	2.6	3280
AMD1_1000	2.6	3120
AMD2_500	2.7	3120
AMD2_50000	2.8	3120

¹ Steady-state SiO₂ levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest SiO₂ levels, respectively.

In summary, the data in this subsection show that low pH values in leaching solutions favor the release of SiO₂ from smectite clays. Thus, pH is a key factor on the release of SiO₂ from the smectite clay and the dissolution of clay in general. Overall, the higher the Fe²⁺, K⁺ and Na⁺ levels in these leaching solutions at pH 2 and 3, the better the coagulation of SiO₂ colloidal particles in my experiments. The better the coagulation of SiO₂ colloidal particles the lower the SiO₂ levels in these leaching solutions at steady-state.

4.2.3 Ferrous iron

The leaching solution termed as AMD1_500 contained initially ferrous iron concentrations of around 500 mg/L. The leaching solution termed as AMD1_1000 contained initially ferrous iron concentrations of around 1000 mg/L. The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L. The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). The ferrous iron levels overtime in these leaching solutions (AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000) at pH of 2 and 3 are shown in Figures 17-18.

The ferrous iron levels in AMD1_500 and AMD1_1000 at pH 2 and 3 decreased fast and sharply in the first 150 hours of leaching, as shown in Figures 17-18, respectively. The ferrous iron levels in AMD1_500 at pH 2 decreased from around 583 mg/L to around 508 mg/L. Likewise, the ferrous iron levels in AMD1_500 at pH 3 decreased from around 559 mg/L to around 406 mg/L. Moreover, the ferrous iron levels in AMD1_1000 at pH 2 decreased from

around 1142 mg/L to around 1037 mg/L. Likewise, the ferrous iron levels in AMD1_1000 at pH 3 decreased from around 1132 mg/L to around 911 mg/L.

After this initial fast and sharp decrease (~150 hours), the ferrous iron levels remained stable overtime in AMD1_500 and AMD1_1000 at pH of 2 and 3 (Figures 17-18). However and despite this stability, the ferrous iron levels in AMD1_500 and AMD1_1000 tended to slightly decrease with time at pH 3 while increasing at pH 2 (Figures 17-18). These data suggest that the smectite structure is fairly stable at pH 3. However, as the pH decreases to 2, structural iron impurities are slowly released from the clay lattice due to the higher degradation of the clay structure at pH of 2. Overall, these data is consistent with the higher Al and SiO₂ levels found in leaching solutions at pH 2 (Figures 13 and 15, respectively) as compared to pH 3 (Figures 14 and 16, respectively).

The ferrous iron levels in AMD2_500 at pH 3 also decreased fast and sharply in the first 150 hours of leaching as shown in Figure 17. Thus, the ferrous iron levels in AMD2_500 at pH 3 decreased from around 548 mg/L to around 444 mg/L. After this initial fast and sharp decrease (~150 hours), the ferrous iron levels remained stable overtime in AMD2_500 at pH 3 (Figure 17). The ferrous iron levels in AMD2_500 at pH of 2 decreased fast and sharply in the first 150 hours of leaching (Figure 17). Thus, the ferrous iron levels in AMD2_500 at pH 2 decreased from around 583 mg/L to around 520 mg/L. After this initial fast and sharp decrease, the ferrous iron levels in AMD2_500 at pH 2 increased slowly overtime. Once the steady-state was achieved, the level of ferrous iron in AMD2_500 at pH 2 was around 570 mg/L as shown in Table 17. The increase of ferrous iron overtime in AMD2_500 at pH 2 is likely due to the slow release of structural iron impurities from the clay lattice due to the higher degradation of the clay structure at pH of 2.

The ferrous iron levels in AMD2_50000 at pH 3 remained fairly stable throughout the experiment and within 5% of the initial ferrous iron levels (434 mg/L) (Figure 17). Thus, the decrease of ferrous iron levels in AMD2_50000 at pH 3 and overtime was minor. Once the steady-state was achieved, the level of ferrous iron in AMD2_50000 at pH 3 was around 428 mg/L as shown in Table 18. The ferrous iron levels in AMD2_50000 at pH 2 decreased to around 460 mg/L in the first 150 hours. After that, the ferrous iron levels increased slowly overtime, and eventually surpassed the initial values of ferrous iron (480 mg/L) once steady-state (~500 mg/L) (Table 17) was reached. This high steady-state ferrous iron level (~500 mg/L) in AMD2_50000 is likely due to the release of iron impurities from the structure of smectite which is more degraded at these pH values of 2.

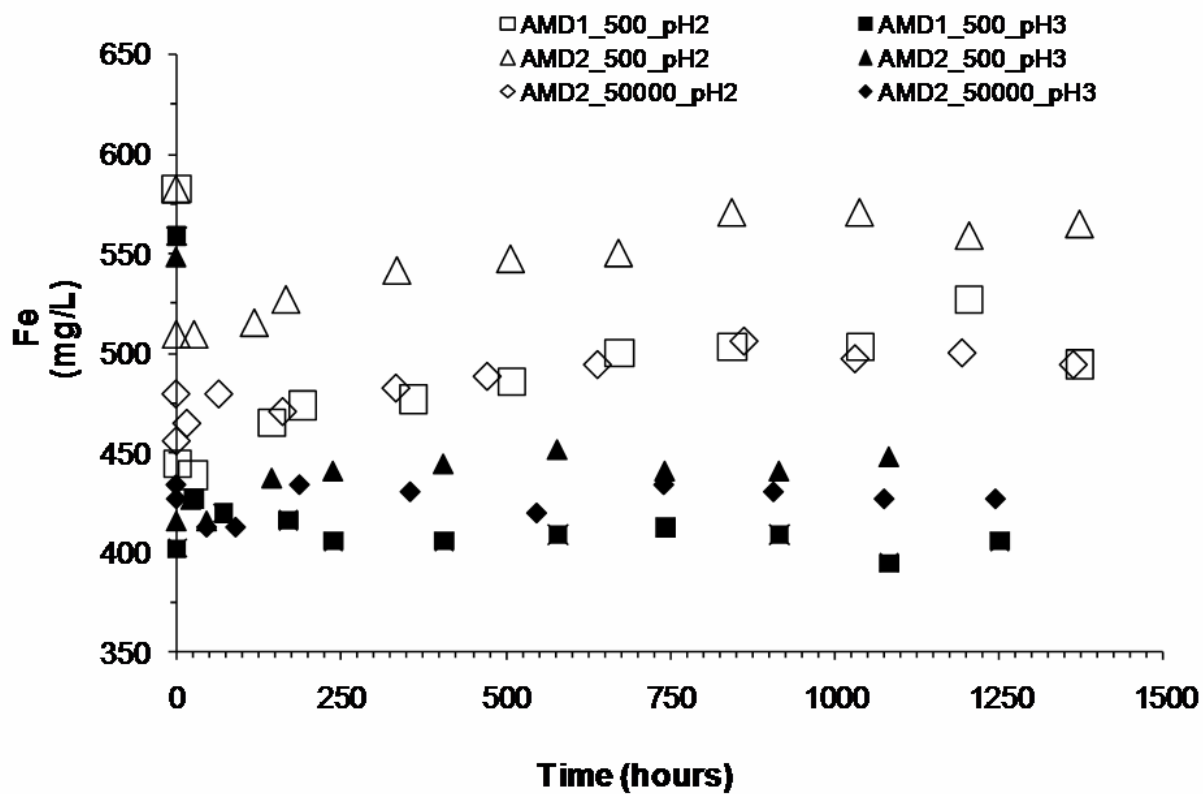


Figure 17. Levels of iron vs. time in AMD1_500, AMD2_500 and AMD2_50000 at pH 2 and 3

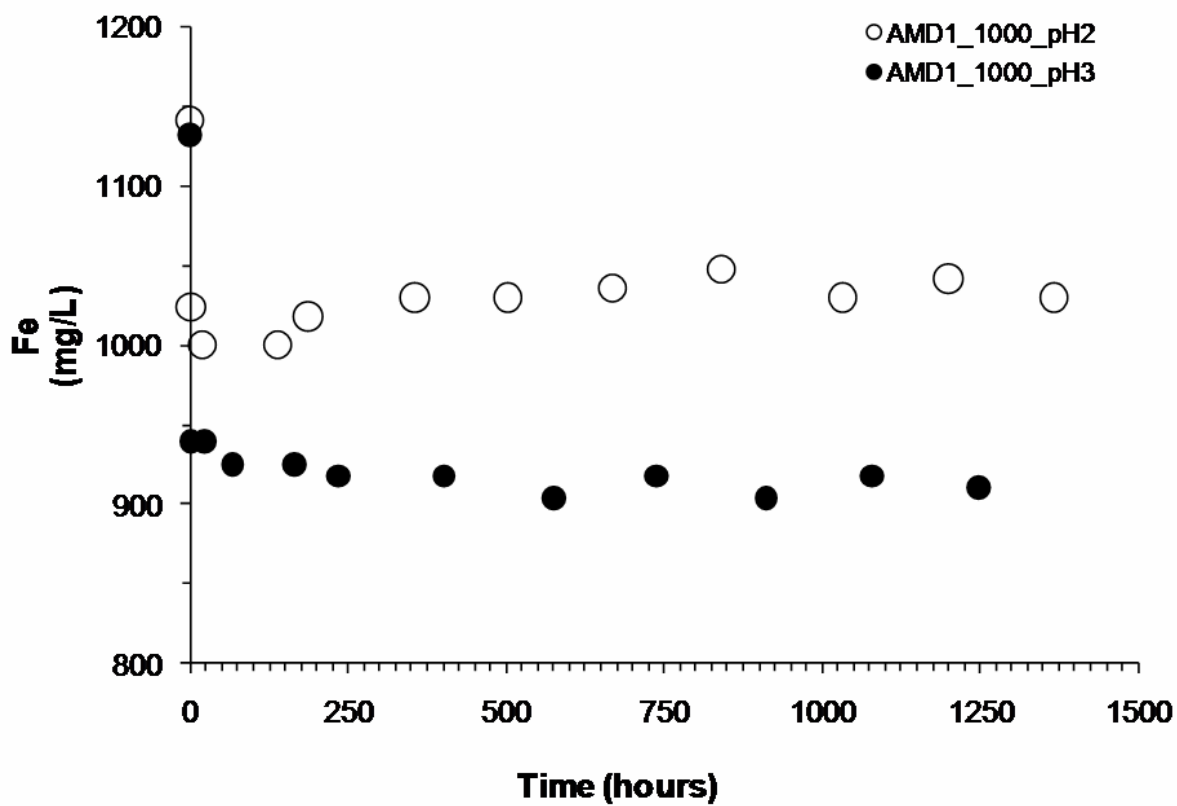


Figure 18. Levels of iron vs. time in AMD1_1000 at pH 2 and 3

Table 17. The steady-state pH and ferrous iron levels in the different leaching solutions at initial pH 2

Leaching solution	pH	¹Fe²⁺ (mg/L)
D.W.	3.2	² <2
Sulfuric acid	2.0	20.3
AMD1_500	2.0	508
AMD1_1000	2.0	1037
AMD2_500	2.0	565
AMD2_50000	2.1	499

¹ Steady-state Fe levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest Fe levels, respectively. ² Practical quantitation limit (PQL) was 2 mg/L for Fe.

Table 18. The steady-state pH and ferrous iron levels in the different leaching solutions at initial pH 3

Leaching solution	pH	¹Fe²⁺ (mg/L)
Sulfuric acid	2.9	² <2
AMD1_500	2.6	406
AMD1_1000	2.6	911
AMD2_500	2.7	444
AMD2_50000	2.8	428

¹ Steady-state Fe levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest Fe levels, respectively. ² Practical quantitation limit (PQL) was 2 mg/L for Fe.

In summary, the data in this subsection show that overall, initial high levels of ferrous iron in leaching solutions at pH 2 and 3 decreased fast and sharply in the first 150 hours of leaching. The ferrous iron levels in these leaching solutions at pH 2 increased slowly overtime after the first 150 hours of leaching. However, the ferrous iron levels in leaching solutions at pH 3 remained rather stable overtime after the first 150 hours of leaching. This suggests that, lower pH values of 2 enhance the release of structural iron impurities from the clay lattice. This is consistent with the higher Al and SiO₂ levels found in leaching solutions at pH 2 as compared to pH 3. All these trends support that the smectite structure is more degraded at low pH of 2.

4.2.4 Potassium

The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L. The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). The potassium levels overtime in these leaching solutions (AMD2_500 and AMD2_50000) at pH of 2 and 3 are shown in Figures 19-20.

The potassium levels in AMD2_500 at pH 3 decreased fast and sharply in the first 150 hours of leaching, as shown in Figure 19. The potassium levels in AMD2_500 at pH 3 decreased from around 448 mg/L to around 405 mg/L. The potassium levels in AMD2_500 at pH 2 tended to decrease in the first 150 hours of leaching (Figure 19). After this initial decrease, the potassium levels remained rather stable with time and were consistently within 5% of the initial potassium levels (420 mg/L) in AMD2_500 at pH 2. The potassium levels in AMD2_500 at pH 2 reached around 402 mg/L at steady state (Table 19). Thus, the decrease of potassium levels in

AMD2_500 at pH 2 was minor. At this low pH values of 2, the smectite structure is more degraded as compared to pH values of 3. Thus, the cation exchange capacity of the clay may be reduced, limiting the extent of sorption of potassium from the leaching solution into the clay solid phase.

The potassium levels in AMD2_50000 at pH 2 and 3 were rather scattered overtime. However, by inspection of Figure 20 it appears that the potassium levels in AMD2_50000 at pH 2 and 3 tended to decrease overtime. The initial decrease in potassium levels (in the first 150 hours) was within 5% of the initial potassium levels: 45291 mg/L in AMD2_50000 at pH 2 and 45111 mg/L in AMD2_50000 at pH 3. Once the steady-state was achieved, the levels of potassium were around 43800 mg/L in both AMD2_50000 at pH 2 and 3 (Tables 19-20).

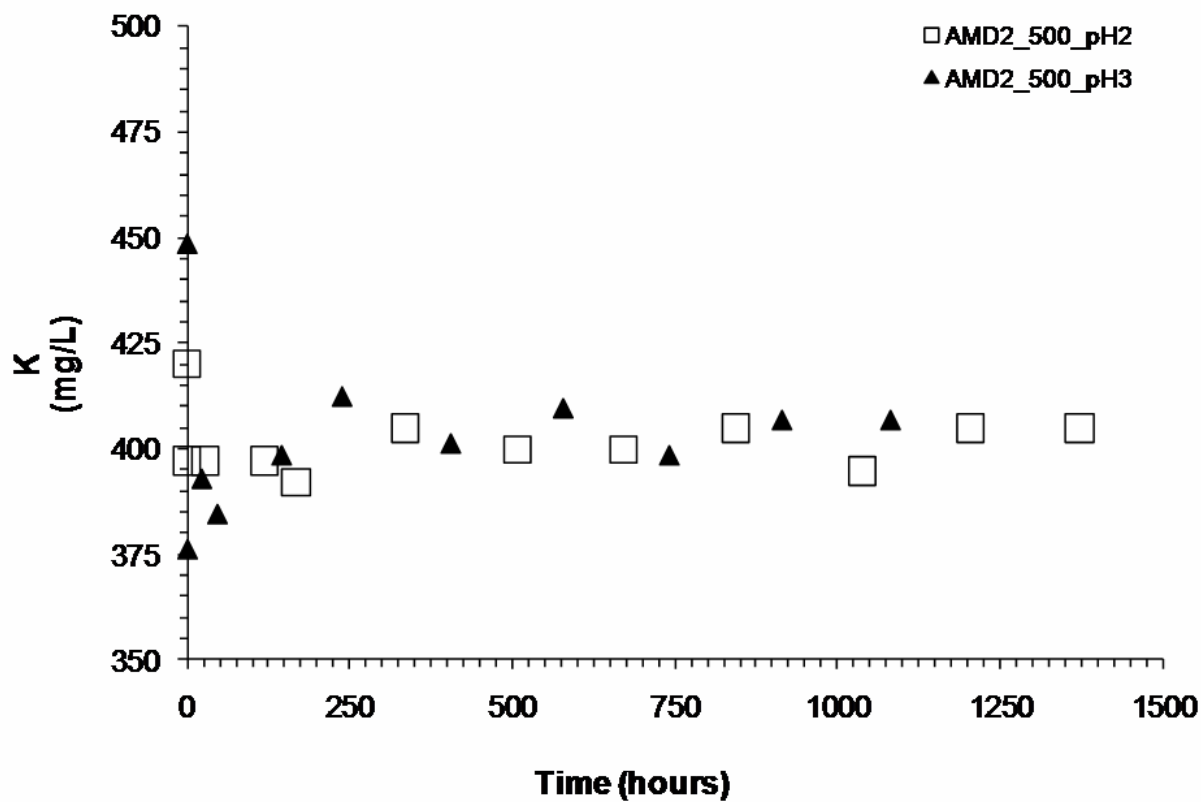


Figure 19. Levels of potassium vs. time in AMD2_500 at pH 2 and 3

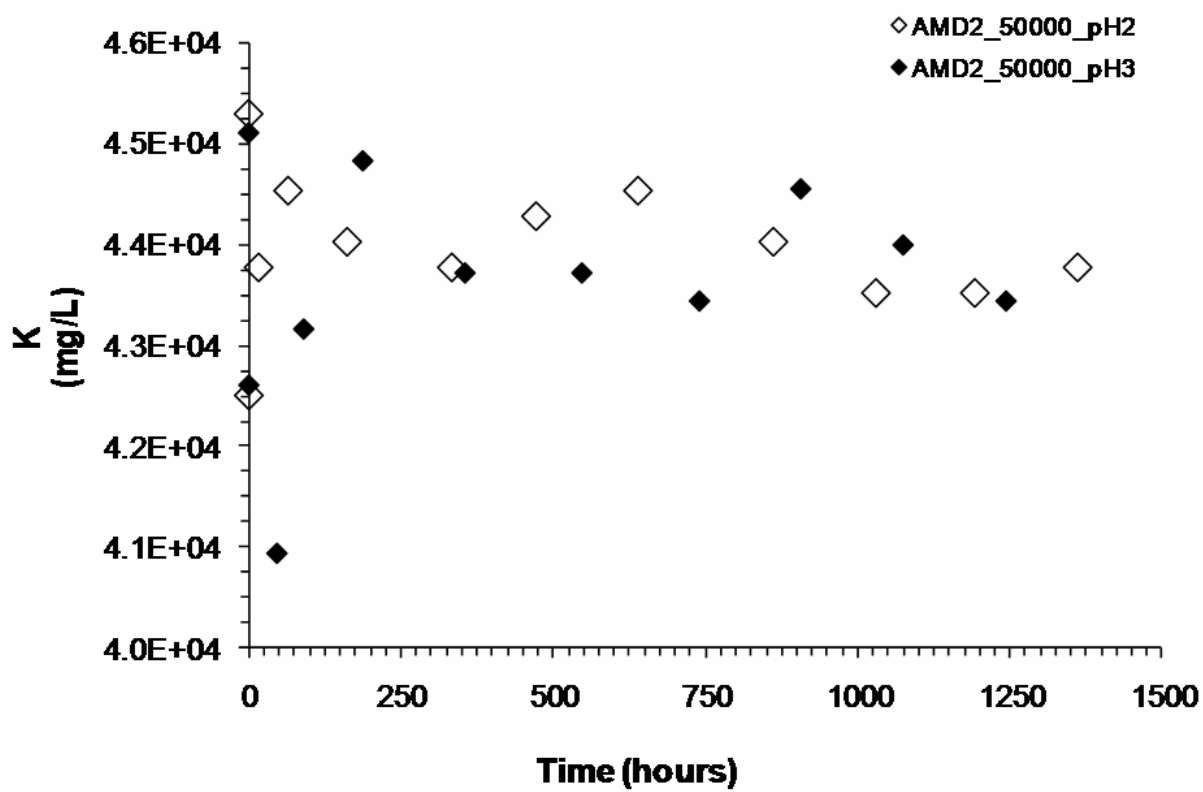


Figure 20. Levels of potassium vs. time in AMD2_50000 at pH 2 and 3

Table 19. The steady-state pH and potassium levels in the different leaching solutions at initial pH 2

Leaching solution	pH	¹K⁺ (mg/L)
D.W.	3.2	² <2
Sulfuric acid	2.0	2.7
AMD1_500	2.0	2.3
AMD1_1000	2.0	² <2
AMD2_500	2.0	402
AMD2_50000	2.1	43709

¹ Steady-state K levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest K levels, respectively. ² Practical quantitation limit (PQL) was 2 mg/L for K.

Table 20. The steady-state pH and potassium levels in the different leaching solutions at initial pH 3

Leaching solution	pH	¹K⁺ (mg/L)
Sulfuric acid	2.9	² <2
AMD1_500	2.6	² <2
AMD1_1000	2.6	² <2
AMD2_500	2.7	405
AMD2_50000	2.8	43833

¹ Steady-state K levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest K levels, respectively. ² Practical quantitation limit (PQL) was 2 mg/L for K.

In summary, the data in this subsection show that overall, the initial high levels of potassium in leaching solutions at pH 2 and 3 decreased fast and sharply in the first 150 hours of leaching. The extent of decrease of potassium in these leaching solutions was higher at pH 3 than at pH 2. At low pH values of 2, the smectite structure is more degraded as compared to pH values of 3. Thus, the cation exchange capacity of the clay may be reduced, limiting the extent of sorption of potassium from the leaching solution into the clay solid phase.

4.2.5 Sodium

The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L. The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). The sodium levels overtime in these leaching solutions (AMD2_500 and AMD2_50000) at pH of 2 and 3 are shown in Figures 21-22.

The sodium levels in AMD2_500 at pH 3 decreased fast and sharply in the first 150 hours of leaching, as shown in Figure 21. Thus, the sodium levels in AMD2_500 at pH 3 decreased from around 851 mg/L to around 803 mg/L. The sodium levels in AMD2_500 at pH 2 were rather scattered overtime. However, by inspection of Figure 21 it appears that the sodium levels in AMD2_500 at pH 2 tended to decrease in the first 150 hours of leaching. This decrease in sodium levels appeared to be within 5% of the initial sodium concentrations (795 mg/L) in AMD2_500 at pH 2. Thus, the decrease of sodium levels in AMD2_500 at pH 2 was minor. At this low pH values of 2, the smectite structure is more degraded as compared to pH values of 3. Thus, the cation exchange capacity of the clay may be reduced, limiting the extent of sorption of

sodium from the leaching solution into the clay solid phase. Once the steady-state was achieved, the level of sodium in AMD2_500 at pH 2 was around 758 mg/L as shown in Table 21.

The sodium levels in AMD2_50000 at pH 2 and 3 were rather scattered overtime. However, by inspection of Figure 22 it appears that the sodium levels in AMD2_50000 at pH 2 and 3 tended to decrease in the first 150 hours of leaching. This decrease in sodium levels was within 5% of the initial sodium concentrations: 45805 mg/L in AMD2_50000 at pH 2 and 48758 mg/L in AMD2_50000 at pH 3. Once the steady-state was achieved, the levels of sodium were around 44600 mg/L in AMD2_50000 at pH 2 and 48300 mg/L in AMD2_50000 at pH 3 (Table 21-22).

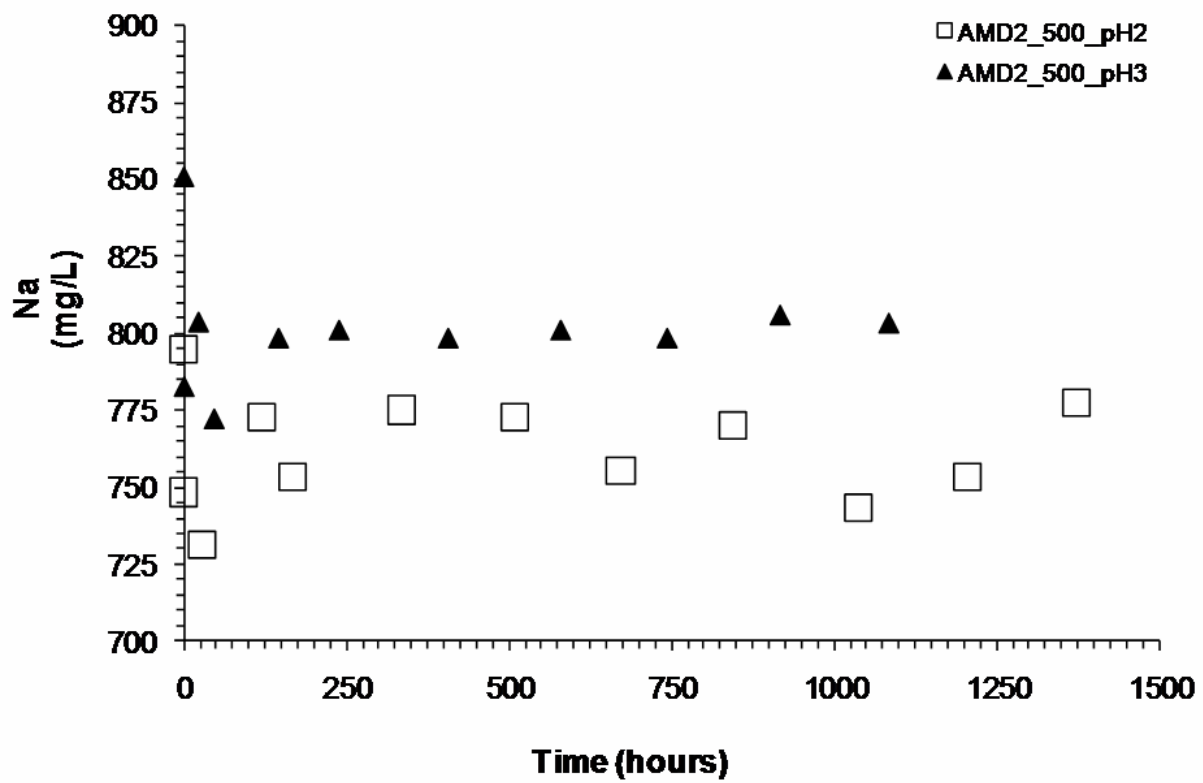


Figure 21. Levels of sodium vs. time in AMD2_500 at pH 2 and 3

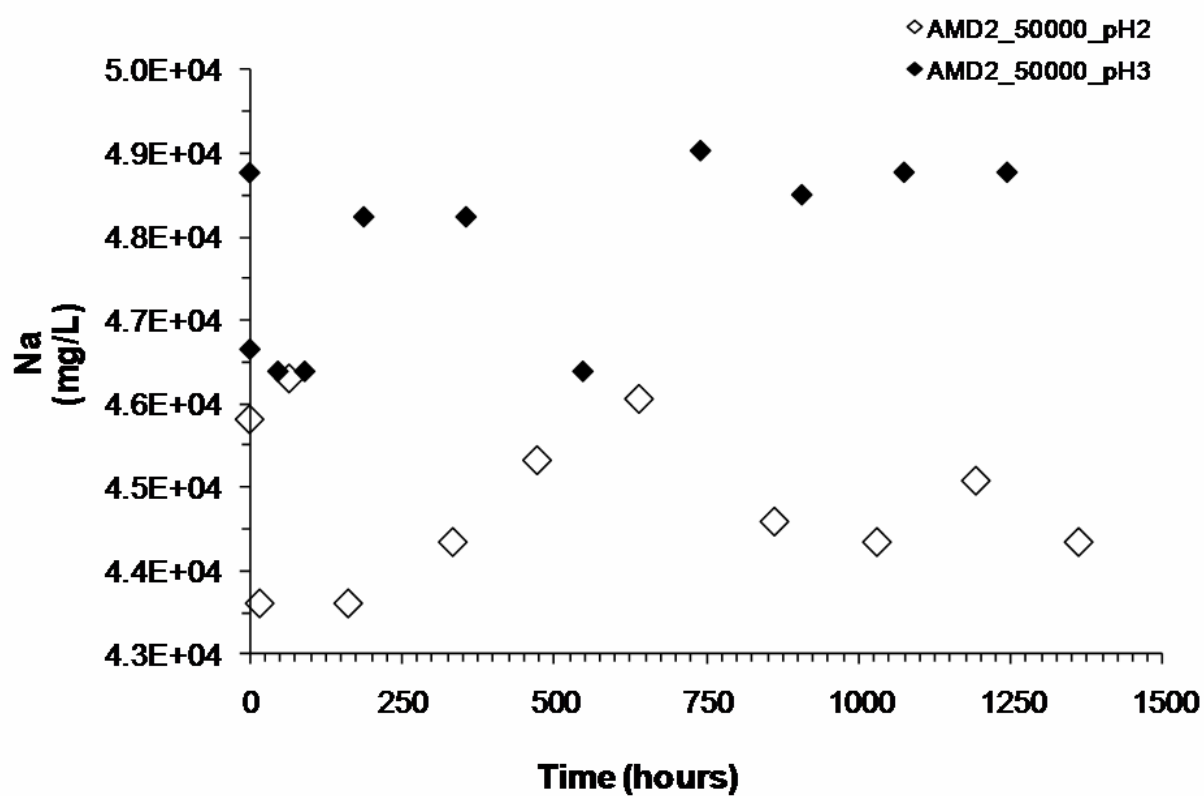


Figure 22. Levels of sodium vs. time in AMD2_50000 at pH 2 and 3

Table 21. The steady-state pH and sodium levels in the different leaching solutions at initial pH 2

Leaching solution	pH	¹Na⁺ (mg/L)
D.W.	3.2	3.5
Sulfuric acid	2.0	4.3
AMD1_500	2.0	5.5
AMD1_1000	2.0	² <2
AMD2_500	2.0	758
AMD2_50000	2.1	44585

¹ Steady-state Na levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest Na levels, respectively. ² Practical quantitation limit (PQL) was 2 mg/L for Na.

Table 22. The steady-state pH and sodium levels in the different leaching solutions at initial pH 3

Leaching solution	pH	¹Na⁺ (mg/L)
Sulfuric acid	2.9	² <2
AMD1_500	2.6	4.9
AMD1_1000	2.6	² <2
AMD2_500	2.7	803
AMD2_50000	2.8	48286

¹ Steady-state Na levels were determined as the average of the last consecutive samples taken at least 1 week apart and within 10% of the highest Na levels, respectively. ² Practical quantitation limit (PQL) was 2 mg/L for Na.

In summary, the data in this subsection show that overall, the initial high levels of sodium in leaching solutions decreased fast and sharply in the first 150 hours of leaching. The extent of decrease of sodium in these leaching solutions was higher at pH 3 than at pH 2. At low pH values of 2, the smectite structure is more degraded as compared to pH values of 3. Thus, the cation exchange capacity of the clay may be reduced, limiting the extent of sorption of sodium from the leaching solution into the clay solid phase.

4.2.6 Cation sorption into smectite clays at pH of 2 and 3

The leaching solution termed as AMD1_500 contained initially ferrous iron concentrations of around 500 mg/L. The leaching solution termed as AMD1_1000 contained initially ferrous iron concentrations of around 1000 mg/L (Table 8). The release of aluminum from the smectite clay to these leaching solutions (AMD1_500 and AMD1_1000) at pH 2 and 3 and in the first 150 hours of leaching was fast. Thus, the levels of Al in AMD1_500 at pH 2 increased from <80 $\mu\text{gAl/g}$ clay (<1 mg/L) to over 1500 $\mu\text{gAl/g}$ clay in the first 150 hours. The levels of Al in AMD1_500 at pH 3 increased from <80 $\mu\text{gAl/g}$ clay (<1 mg/L) to over 850 $\mu\text{gAl/g}$ clay in the first 150 hours. Moreover, the levels of Al in AMD1_1000 at pH 2 increased from <80 $\mu\text{gAl/g}$ clay (<1 mg/L) to over 2100 $\mu\text{gAl/g}$ clay in the first 150 hours. The levels of Al in AMD1_1000 at pH 3 increased from <80 $\mu\text{gAl/g}$ clay (<1 mg/L) to over 1400 $\mu\text{gAl/g}$ clay in the first 150 hours (Figures 13-14).

This initial and rapid release of aluminum was concomitant with a sharp and fast decrease of ferrous iron levels in AMD1_500 and AMD1_1000 at pH 2 and 3 (Figures 17-18). The ferrous iron levels in AMD1_500 at pH 2 decreased from around 583 mg/L to around 508 mg/L.

The ferrous iron levels in AMD1_1000 at pH 2 decreased from around 1142 mg/L to around 1037 mg/L. The ferrous iron levels in AMD1_500 at pH 3 decreased from around 559 mg/L to over 406 mg/L. The ferrous iron levels in AMD1_1000 at pH 3 decreased from around 1132 mg/L to around 911 mg/L. This first stage of fast release (~150 hours) of aluminum with leaching solutions AMD1_500 and AMD1_1000 at pH 2 and 3 suggest that surface exchange reactions took place.

The initial rapid release of Al from smectite clay was followed by a second stage of slower release of Al at a relatively constant rate, giving the appearance of a zero order reaction. In this second stage, the Al levels in AMD1_500 at pH 2 increased slowly from over 1500 $\mu\text{gAl/g}$ clay to around 2000 $\mu\text{gAl/g}$ clay. The Al levels in AMD1_1000 at pH 2 increased slowly from over 2100 $\mu\text{gAl/g}$ clay to around 2600 $\mu\text{gAl/g}$ clay (Figure 13). The Al levels in AMD1_500 at pH 3 increased slowly from over 850 $\mu\text{gAl/g}$ clay to around 900 $\mu\text{gAl/g}$ clay. The Al levels in AMD1_1000 at pH 3 increased slowly from over 1400 $\mu\text{gAl/g}$ clay to around 1600 $\mu\text{gAl/g}$ clay (Figure 14). The SiO_2 levels in these leaching solutions (AMD1_500 and AMD1_1000) at pH 2 and 3 increase gradually overtime. In the long-term, the SiO_2 levels in these leaching solutions (AMD1_500 and AMD1_1000) at pH 2 and 3 increased slowly (Figures 15-16). Both trends observed in the Al and SiO_2 levels in these leaching solutions (AMD1_500 and AMD1_1000) at 2 and 3 are consistent with slow clay dissolution processes dominating the long-term.

The leaching solution termed as AMD2_500 contained initially ferrous iron of around 500 mg/L, potassium of around 500 mg/L and sodium around 1000 mg/L. The leaching solution termed as AMD2_50000 contained initially ferrous iron of around 500 mg/L, potassium of around 50000 mg/L and sodium around 50000 mg/L (Table 8). The release of aluminum from

the smectite clay to these leaching solutions (AMD2_500 and AMD2_50000) at pH 2 and 3 and in the first 150 hours of leaching was fast. Thus, the levels of Al in AMD2_500 at pH 2 increased from $<80 \mu\text{gAl/g clay}$ ($<1 \text{ mg/L}$) to over $2029 \mu\text{gAl/g clay}$ in the first 150 hours. The levels of Al in AMD2_500 at pH 3 increased from $<80 \mu\text{gAl/g clay}$ ($<1 \text{ mg/L}$) to over $1180 \mu\text{gAl/g clay}$ in the first 150 hours. Moreover, the levels of Al in AMD2_50000 at pH 2 increased from $<80 \mu\text{gAl/g clay}$ ($<1 \text{ mg/L}$) to over $1407 \mu\text{gAl/g clay}$ in the first 150 hours. The levels of Al in AMD2_50000 at pH 3 increased from $<80 \mu\text{gAl/g clay}$ ($<1 \text{ mg/L}$) to over $1800 \mu\text{gAl/g clay}$ in the first 150 hours (Figures 13-14).

The initial and rapid release of aluminum from the smectite clay to the AMD2_500 leaching solution at initial pH of 3 was concomitant with a sharp decrease of: ferrous iron concentrations, from around 548 mg/L to around 444 mg/L (Figure 17), potassium concentrations from 448 mg/L to around 405 mg/L (Figure 19) and sodium concentrations from 851 mg/L to around 803 mg/L (Figure 21). This first stage of fast release of aluminum suggests that exchange reactions involving ferrous iron, potassium and sodium in this leaching solution (AMD2_500) at initial pH of 3 and aluminum on the surface of the clay took place within the first hours (~ 150 hours) within the reactor. The initial rapid release of aluminum in AMD2_500 at pH 3 was followed by a second stage of slower release of Al at a relatively constant rate, in the presence of excess clay, giving the appearance of a zero order reaction.

In this second stage, the Al levels in AMD2_500 at pH 3 increased from over $1180 \mu\text{gAl/g clay}$ to around $1400 \mu\text{gAl/g clay}$. The SiO_2 levels in AMD2_500 at pH 3 increased gradually overtime. In the long-term, the SiO_2 levels in AMD2_500 at pH 3 increased slowly (Figure 16). Moreover, Fe^{2+} , K^+ and Na^+ levels in AMD2_500 at pH 3 were rather stable overtime in the long-term. All these trends observed in AMD2_500 at pH 3 suggest that the

release of Al from smectite clays to AMD2_500 at pH 3 is dominated by clay dissolution processes in the long-term.

The decrease of Fe^{2+} (Figure 17), K^+ (Figure 19) and Na^+ (Figure 21) levels in AMD2_500 at pH 2 in the first 150 hours of leaching was smaller if it is compared to that in AMD2_500 at pH 3. The initial levels of these cations (Fe^{2+} , K^+ , Na^+) in AMD2_500 at pH 2 were 583 mg/L (Fe^{2+}), 420 mg/L (K^+) and 795 mg/L (Na^+). The ferrous iron levels in AMD2_500 at pH 2 decreased to around 520 mg/L in the first 150 hours. The potassium levels in AMD2_500 at pH 2 decreased to around 395 mg/L in the first 150 hours. The sodium levels in AMD2_500 at pH 2 decreased to around 760 mg/L in the first 150 hours. The decrease of these cations (Fe^{2+} , K^+ , Na^+) in the first 150 hours of leaching was concomitant with the sharp and fast release of Al in AMD2_500 at pH 2. This first stage of fast release (~150 hours) of Al in AMD2_500 at pH 2 suggests that surface exchange reactions took place.

The initial rapid release of aluminum in AMD2_500 at pH 2 was followed by a second stage of slower release of Al at a relatively constant rate, in the presence of excess clay, giving the appearance of a zero order reaction.

In this second stage, the Al levels in AMD2_500 at pH 2 increased from around 2029 $\mu\text{gAl/g}$ clay to around 2700 $\mu\text{gAl/g}$ clay. The SiO_2 levels in AMD2_500 at pH 2 increased gradually overtime. In the long-term, the SiO_2 levels in AMD2_500 at pH 2 increased slowly (Figure 15). In this second stage, the iron levels in AMD2_500 at pH 2 increased slowly overtime likely due to the release of iron impurities from the smectite structure as this low pH of 2. The K^+ levels in AMD2_500 at pH 2 were rather stable overtime in the long-term. The Na^+ levels in AMD2_500 at pH 2 were rather scattered and varied overtime between around around

775 mg/L and 730 mg/L in the long-term. All these trends observed in AMD2_500 at pH 2 suggest that the release of Al from smectite clays to AMD2_500 at pH 2 is dominated by clay dissolution processes in the long-term.

The decrease of Fe^{2+} (Figure 17), K^+ (Figure 20) and Na^+ (Figure 22) levels in AMD2_50000 at pH 2 in the first 150 hours was within 5% of the initial Fe^{2+} (480 mg/L), K^+ (45291 mg/L) and Na^+ (45805 mg/L) levels in AMD2_50000 at pH 2. Thus, the ferrous iron levels in AMD2_50000 at pH 2 decreased to around 460 mg/L in the first 150 hours. The potassium levels in AMD2_50000 at pH 2 decreased to around 43800 mg/L in the first 150 hours. The sodium levels in AMD2_50000 at pH 2 decreased to around 44600 mg/L in the first 150 hours. The decrease of these cations (Fe^{2+} , K^+ , Na^+) in the first 150 hours of leaching was concomitant with the sharp and fast release of Al in AMD2_50000 at pH 2. This first stage of fast release (~150 hours) of Al in AMD2_50000 at pH 2 suggests that surface exchange reactions took place.

The initial rapid release of aluminum in AMD2_50000 at pH 2 was followed by a second stage of slower release of Al at a relatively constant rate, in the presence of excess clay, giving the appearance of a zero order reaction.

In this second stage, the Al levels in AMD2_50000 at pH 2 increased from around 1407 $\mu\text{gAl/g}$ clay to around 2100 $\mu\text{gAl/g}$ clay. The SiO_2 levels in AMD2_50000 at pH 2 increased gradually overtime. In the long-term, the SiO_2 levels in AMD2_50000 at pH 2 increased slowly (Figure 15). In this second stage, the iron levels in AMD2_50000 at pH 2 increased slowly overtime likely due to the release of iron impurities from the smectite structure as this low pH of 2. The K^+ levels in AMD2_50000 at pH 2 were rather scattered and varied overtime between

around 43500 mg/L and 44500 mg/L in the long-term. The Na^+ levels in AMD2_50000 at pH 2, were rather scattered and varied overtime between around 44300 mg/L and 46000 mg/L in the long-term. All these trends observed in AMD2_50000 at pH 2 suggest that the release of Al from smectite clays to AMD2_50000 at pH 2 is dominated by clay dissolution processes in the long-term.

The decrease of Fe^{2+} (Figure 17), K^+ (Figure 20) and Na^+ (Figure 22) levels in AMD2_50000 at pH 3 in the first 150 hours was within 5% of the initial Fe^{2+} (434 mg/L), K^+ (45111 mg/L) and Na^+ (48758 mg/L) levels in AMD2_50000 at pH 3 as well. Thus, the ferrous iron levels in AMD2_50000 at pH 3 decreased to around 428 mg/L in the first 150 hours. The potassium levels in AMD2_50000 at pH 3 decreased to around 43800 in the first 150 hours. The sodium levels in AMD2_50000 at pH 3 decreased to around 48300 mg/L in the first 150 hours. The decrease of these cations (Fe^{2+} , K^+ , Na^+) in the first 150 hours of leaching was concomitant with the sharp and fast release of Al in AMD2_50000 at pH 3. This first stage of fast release (~150 hours) of Al in AMD2_50000 at pH 3 suggests that surface exchange reactions took place.

The initial rapid release of aluminum in AMD2_50000 at pH 3 was followed by a second stage of slower release of Al at a relatively constant rate, in the presence of excess clay, giving the appearance of a zero order reaction.

In this second stage, the Al levels in AMD2_50000 at pH 3 increased from around 1800 $\mu\text{gAl/g}$ clay to around 2100 $\mu\text{gAl/g}$ clay. The SiO_2 levels in AMD2_50000 at pH 3 increase gradually overtime. In the long-term, the SiO_2 levels in AMD2_50000 at pH 3 increased slowly (Figure 16). In this second stage the iron levels in AMD2_50000 at pH 3 remained rather stable overtime. The K^+ levels in AMD2_50000 at pH 3 were rather scattered and varied overtime

between around 43400 mg/L and 44800 mg/L in the long-term. The Na^+ levels in AMD2_50000 at pH 2 were rather scattered and varied overtime between around 46400 mg/L and 49000 mg/L in the long-term. All these trends observed in AMD2_50000 at pH 3 suggest that the release of Al from smectite clays to AMD2_50000 at pH 3 is dominated by clay dissolution processes in the long-term.

The net sorption and release of these and other measured cations (H^+ , Al^{3+} , Fe^{2+} , K^+ , Na^+ , Mg^{2+} and Mn^{2+}) in each one of the leaching solutions at initial pH of 2 and 3 and at steady-state are summarized in Table 23. The election of these cations (H^+ , Al^{3+} , Fe^{2+} , K^+ , Na^+ , Mg^{2+} and Mn^{2+}) was made accordingly to the average composition of the exchange phase as well as the structure composition of common acid smectite clay soils. An overall balance of cations sorbed and released to our leaching solutions was attempted. The overall unbalance in leaching solutions containing extreme concentrations of K^+ and Na^+ (AMD2_50000 at pH 2 and 3), as shown in Table 23, was consistent with the precipitation of secondary solid phases. The sorption of K^+ and Na^+ as compared to the release of Al^{3+} per gram of clay in AMD2_50000 at pH of 2 and 3 is significant (Table 23). These data suggest that the mechanism behind the major decrease of K^+ and Na^+ levels in AMD2_50000 at pH 2 and 3 is not exchange but precipitation of secondary solid phases that may incorporate aluminum. The precipitation of these secondary solid phases is consistent with the lower than expected Al levels in AMD2_50000 at pH 2 and 3 found at steady-state (Tables 13-14).

Table 23. Cation sorption/leaching to/from smectite clays from/to leaching solutions at steady-state and initial pH from 2 to 3

	Cation sorption (µeq/g)								
Leaching solution	H ⁺	Al ³⁺	Fe ²⁺	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Mn ²⁺	Overall unbalance
Initial pH ~ 2									
Sulfuric acid	165	121	58	6	15	25.9	40	0	430
AMD1_500	165	238	-215	5	19.1	19.6	50.7	0	282
AMD1_1000	165	294	-301	0	0	19.6	57.9	0	235
AMD2_500	0	296	-52	-37	-129	12.4	50.7	0	142
AMD2_50000	0	235	54	-3237	-4243	-35.5	53.3	0	-7173
Initial pH ~ 3									
Deionized water (D.W.)	50.3	0	0	2	-2.4	-40.7	0	0	9
Sulfuric acid	-26.1	0	0	0	0	-1.6	0	0	-28
AMD1_500	150	105	-439	0	8	2.4	44.8	0	-128
AMD1_1000	137	190	-634	0	0	7.2	46.1	0	-253
AMD2_500	109.1	153	-298	-88	-167	7.6	44.8	0	-239
AMD2_50000	63.2	232	-17.2	-2615	-1642	-33.9	40.8	6.4	-3965

Negative values are $\mu\text{eq/g}$ sorbed from the leaching solution to the smectite clay. Positive values are $\mu\text{eq/g}$ released from the smectite clays to the leaching solution.

Comparison of results with the literature

The exchange of Fe^{2+} with other cations such, as sodium or calcium, on the surface complex of smectite clays has been previously reported by Charlet et al. (2005) and Lantenois et al. (2005).

A conceptual model proposed by Lantenois et al. (2005) explained the destabilization of

dioctahedral smectites as a result of their interaction with metal Fe at realistic temperatures in the context of nuclear waste disposal (80°C). This model relies on the existence of high (basic) pH conditions that result in the deprotonation of OH-groups in smectite and further oxidation of Fe^0 to Fe^{2+} (Fe^0 acting as a proton acceptor). This step is followed by sorption of Fe^{2+} cations on the edges of smectite particles which present high affinity for this cation (Charlet et al., 2005; Lantenois et al., 2005). Although the experiments in this research, conducted at acidic conditions (initial pH of 2 and 3) and temperature of 25°C, differed from those conditions in the study of Lantenois et al. (2005), the exchange of Fe^{2+} with aluminum on the smectite surface suggested in this PhD research is in agreement with the conceptual model proposed by Lantenois et al. (2005).

Part of the cations, including aluminum, previously released from the smectite clay to the AMD may be re-adsorbed and re-incorporated into the aluminosilicate inter-layer to counteract its high CEC (Sondi et al., 2008). Thus, the relatively higher concentrations of aluminum in the leaching solutions containing initial high concentrations of ferrous iron, potassium and sodium as compared to the sulfuric acid leaching solutions may be the result of the exchange of these cations (Fe^{2+} , K^+ and Na^+) with aluminum in the surface complex of smectites.

In a recent work, Shaw et al. (2009) studied the mineralogical alteration of smectite-rich and other clays after leaching with H_2SO_4 solutions at wt/wt clay to solution ratios of 1:20 and pH values between 5 and less than 0. Based on their results, Shaw et al. (2009) presented a conceptual model of the impact of H_2SO_4 on these clays where cations are mobilized from the aluminosilicate inter-layer by substitution reactions with H^+ ions from the H_2SO_4 solution. As the pH decreases to between 3 and 1 the Al-octahedral and Si-tetrahedral layers undergo dissolution. The exchange and dissolution processes suggested in this PhD research as the major mechanisms

of release of aluminum after leaching of smectite clays with synthetic AMD and sulfuric acid at initial pH values of 2 and 3 appear to be consistent with the conceptual model of Shaw et al. (2009).

In summary, the data in this subsection suggest that overall, the initial release of Al from smectite clays to leaching solutions containing Fe^{2+} , K^+ and Na^+ at pH 2 and 3, is dominated by surface exchange reactions. In the long-term, the release of Al from smectite clays to these leaching solutions is dominated by the dissolution of the smectite clay structure.

Ion exchange was assumed to be the main mechanism of release of Al from the clay to leaching solutions containing extreme levels of K^+ and Na^+ (~50000 mg/L, respectively) at pH 2 and 3. A balance between the species released and sorbed to the smectite surface was attempted. The results of this balance showed an overall unbalance in these leaching solutions at pH 2 and 3 consistent with the precipitation of secondary solid phases containing Al.

4.2.7 Levels of Al/Si molar ratio overtime at pH of 2 and 3

There was not previous characterization of the smectite clay used in these batch experiments and thus its structural formula was not known. Thus, the structural formula for smectite clay described by Parkhurst and Appelo (1999) in Equation 2 was used to approach the smectite clay used in these leaching experiments. The theoretical molar Al/Si ratio in the congruent dissolution reaction of smectite clay ($\text{Na}_{0.33}\text{Mg}_{0.33}\text{Al}_{1.67}\text{Si}_4\text{O}_{10}(\text{OH})_2$) as defined by Equation 2 is 0.42. Congruent dissolution means that the dissolution of smectite clay proceeds without the formation of secondary solid phases as shown in Equation 2.

The theoretical molar Al/Si ratio of 0.42 was compared against the molar Al/Si ratios found in these leaching experiments. Thus, the experimental molar ratios of Al/Si in each leaching solution at pH 2 and 3 were plotted versus the leaching time in Figures 23-24. The theoretical molar Al/Si ratio of 0.42 was also included in Figures 23-24. The comparison of these experimental molar Al/Si ratios with the theoretical molar Al/Si ratio allows discriminating the preferential release of these elements (Al and Si) in each leaching solution and overtime.

In general, the experimental Al/Si molar ratio in all leaching solutions decreased overtime approaching a constant value at steady-state as shown in Figures 23-24. The experimental molar Al/Si ratio in sulfuric acid at pH 2 reached around 0.26 at steady state. The experimental molar Al/Si ratio in AMD1_500 at pH 2 reached around 0.61 at steady state. The experimental molar Al/Si ratio in AMD1_500 at pH 3 reached around 0.65 at steady state. The experimental molar Al/Si ratio in AMD1_1000 at pH 2 reached around 0.86 at steady state. The experimental molar Al/Si ratio in AMD1_1000 at pH 3 reached around 1.21 at steady state. The experimental molar Al/Si ratio in AMD2_500 at pH 2 reached around 0.80 at steady state. The experimental molar Al/Si ratio in AMD2_500 at pH 3 reached around 0.98 at steady state. The experimental molar Al/Si ratio in AMD1_50000 at pH 2 reached around 1.20 at steady state. The experimental molar Al/Si ratio in AMD1_50000 at pH 3 reached around 1.45 at steady state.

The release of aluminum from smectites leached with sulfuric solutions at initial pH of 3 was non-detected and thus the molar Al/Si ratio could not be evaluated. In general, the initial release of aluminum (moles/L) was always higher than the silicon in all the leaching solutions at initial pH of 2 and 3, as indicated by Al/Si molar ratios higher than 1. The only exception where it did not take place was in the acid sulfuric leaching solutions at pH 3. Overtime and once steady-state was approached, the Al/Si molar ratios approached or decreased below 1 in most

leaching solutions at initial pH of 2 and 3, as shown in Figures 23-24. The major exception to this trend took place in the AMD2_50000 leaching solutions at pH 2 and 3, where the steady-state experimental molar Al/Si ratio was over 1.

The initial high Al/Si ratios in the leaching solutions initially containing different concentrations of ferrous iron, potassium and sodium at pH 2 and 3 within the first 150 hours of leaching time are consistent with the release of aluminum from the surface of smectite clays due to exchange reactions taking place in the first hours of leaching.

The experimental Al/Si molar ratios in sulfuric acid at pH 2 (Figure 23) better approached the theoretical Al/Si molar ratio of smectite once this system reached steady-state conditions. The steady-state Al/Si ratio in sulfuric acid leaching solutions at initial pH of 2 was slightly lower than the theoretical Al/Si ratio, suggesting to some extent a preferential retention of aluminum over silicon but still close to congruent dissolution, as shown in Figure 23. A similar behavior has been previously reported by Sondi et al. (2008).

Other authors, however, have reported congruent dissolution in acid solutions at these pH 2 values but at temperatures of 50°C and 70 °C (Rozalen et al., 2009). The decrease of the Al/Si ratios below the theoretical Al/Si molar ratio in the sulfuric acid solution at initial pH of 2 could be due to secondary precipitation of Al-phases or to readsorption of aluminum by the smectite surface. Thus, in the absence of cations, such as ferrous iron, potassium and sodium, in the sulfuric leaching solution, to exchange with aluminum on the smectite surface, release of silicon dominates over aluminum. This release of silicon in smectites has been suggested to be driven by dissolution processes from chemically less reactive, but preponderant basal siloxane surfaces on smectite clays (Sondi et al., 2008).

The experimental steady-state Al/Si molar ratios in the rest of leaching solutions (AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000) at pH 2 and 3 were higher than that in the sulfuric acid at pH 2. This is the result of the presence of cations (Fe^{2+} , K^+ and Na^+) in leaching solutions. These cations (Fe^{2+} , K^+ and Na^+) may exchange with Al in the surface of smectite resulting in higher steady-state Al/Si molar ratios as compared to those in sulfuric acid leaching solutions at the same pH.

The experimental steady-state Al/Si molar ratios in the rest of leaching solutions (AMD1_500, AMD1_1000, AMD2_500 and AMD2_50000) at pH 2 and 3 were also higher than the theoretical Al/Si molar ratio of smectite (0.42). These leaching solutions showed a preferential release of aluminum overtime, as indicated Al-Si molar ratios higher than the theoretical Al/Si molar ratio (Figures 23-24). Overall, the extent of preferential release of aluminum followed a decreasing order of steady-state Al/Si molar ratios in leaching solutions at both initial pH of 2 and 3 as followed:

$$\text{AMD2_50000} > \text{AMD1_1000} \geq \text{AMD2_500} > \text{AMD1_500} \quad (17)$$

Overall, the results in Equation 17 suggest that the higher the ferrous iron, potassium and sodium levels in AMD/ARD the higher the deviation from congruent dissolution in the long-term. This is consistent with the formation of secondary solid phases in leaching solutions containing extreme concentrations of Fe^{2+} , K^+ and Na^+ , such as in the case of AMD2_50000 at pH 2 and 3.

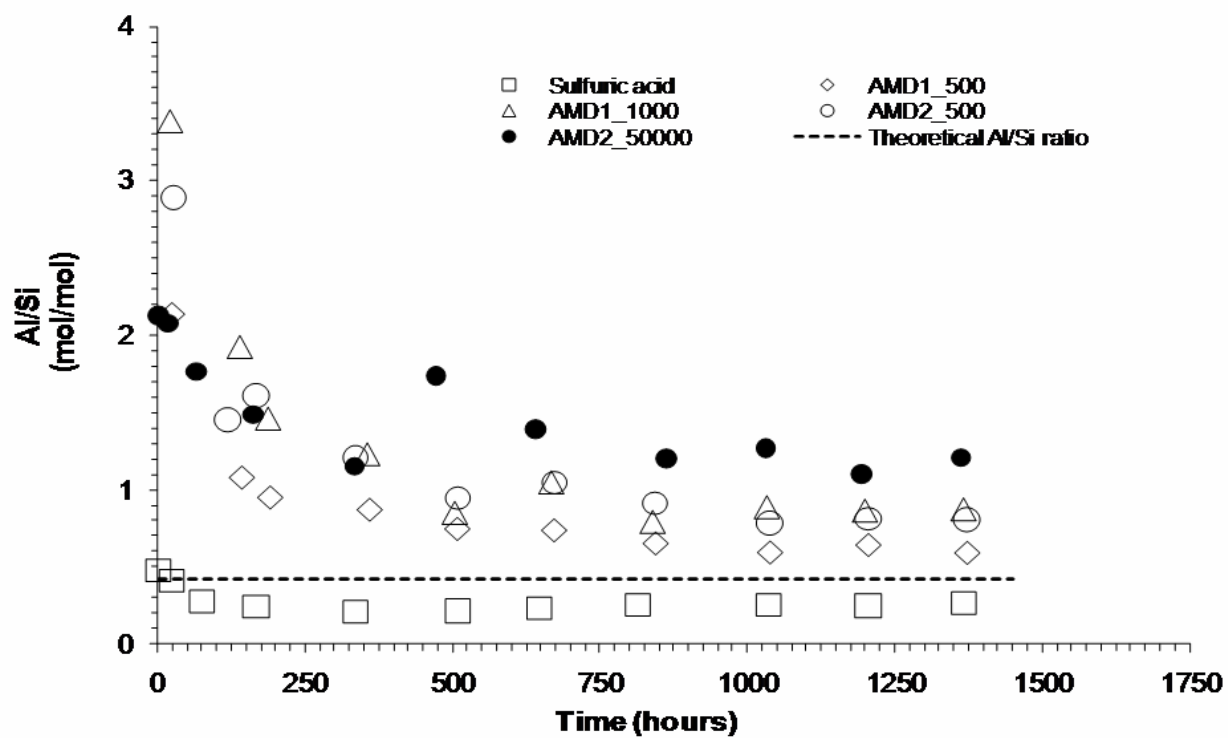


Figure 23. Levels of the Al/Si ratio in leaching experiments of smectite at pH 2

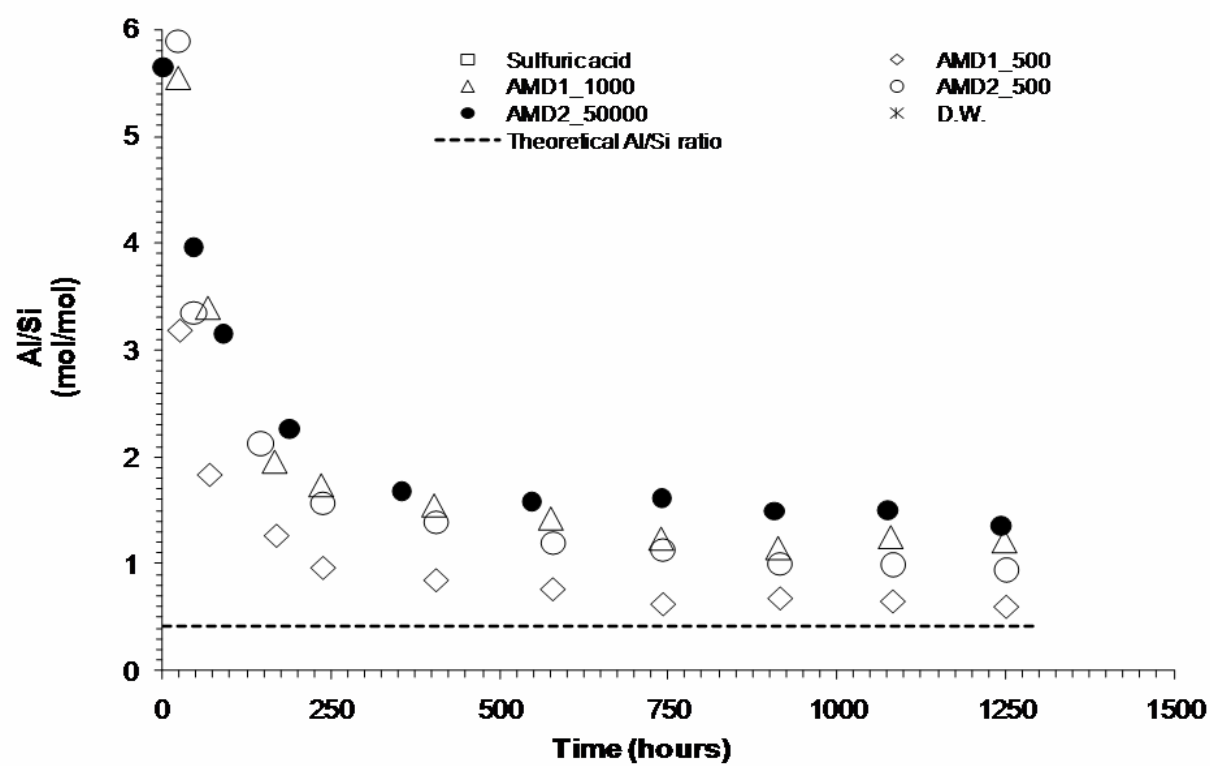


Figure 24. Levels of the Al/Si ratio in leaching experiments of smectite at pH 3

In summary, the data in this subsection support that overall the initial release of Al from smectite clays to leaching solutions containing Fe^{2+} , K^+ and Na^+ at pH 2 and 3, is dominated by surface exchange reactions. The release of Si and Al from smectite clays to these leaching solutions tends to be driven by clay dissolution processes in the long-term. The higher the Fe^{2+} , K^+ and Na^+ levels in these leaching solutions the higher the deviation from congruent dissolution in the long-term. This is consistent with the formation of secondary solid phases that may contain Al, in these leaching solutions containing extreme concentrations of Fe^{2+} , K^+ and Na^+ .

4.2.8 Developed equilibrium relationships from leaching of smectite clays

The steady-state levels of Al leached from smectite clay as a function of the initial Fe^{2+} and Na^+ concentrations in leaching solutions at pH of 2 and 3 are shown in Figures 25-26. The formulas shown in these figures represent the best fit of the experimental data. The developed formulas may assist in the determination of estimates of Al levels leached per gram of smectite clays, which are frequently found in AMD/ARD affected sites. Thus, the estimates of Al per gram of clay may be determined as a function of the initial concentrations of Fe^{2+} and Na^+ levels found in the field AMD/ARD.

The steady-state levels of Fe^{2+} sorbed per gram of smectite clay and as a function of the steady-state levels of Fe^{2+} in the leaching solutions containing only Fe^{2+} at pH 2 and 3 are shown in Figure 27. The formulas shown in these figures represent the best fit of our experimental data. Overall, the sorption of Fe^{2+} per gram of clay is higher at pH 3 than at pH 2 as shown in Figure 27. Overall, this reduction in the sorption of Fe^{2+} per gram of clay is concomitant with a higher release of Al and SiO_2 levels in leaching solutions at pH 2 as compared to pH 3. This is

consistent with the higher chemical degradation of smectite at pH 2 than at pH 3. This higher chemical degradation at pH 2 of the smectite structure may affect the exchange capacity of the clay. Consequently, the extent of sorption of Fe^{2+} from the leaching solution to the surface of the smectite clay may be reduced at pH 2 as compared to pH 3 (as shown in Figure 27).

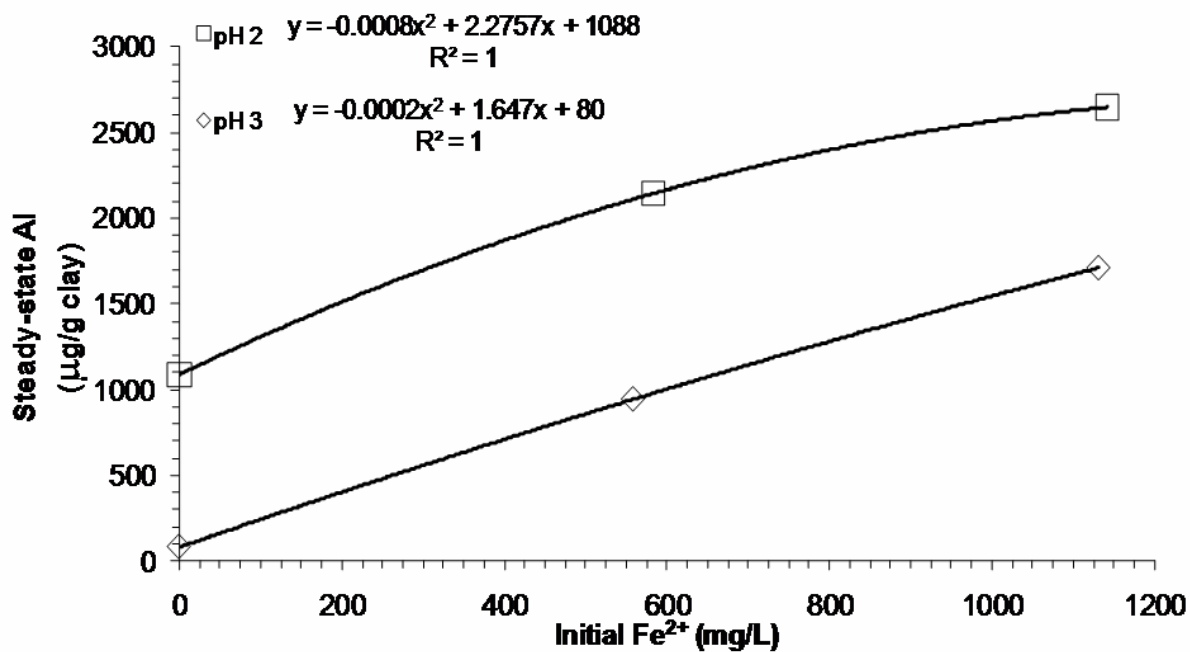


Figure 25. The steady-state levels of Al leached per gram of smectite clay and as a function of the initial ferrous iron levels in the leaching solutions

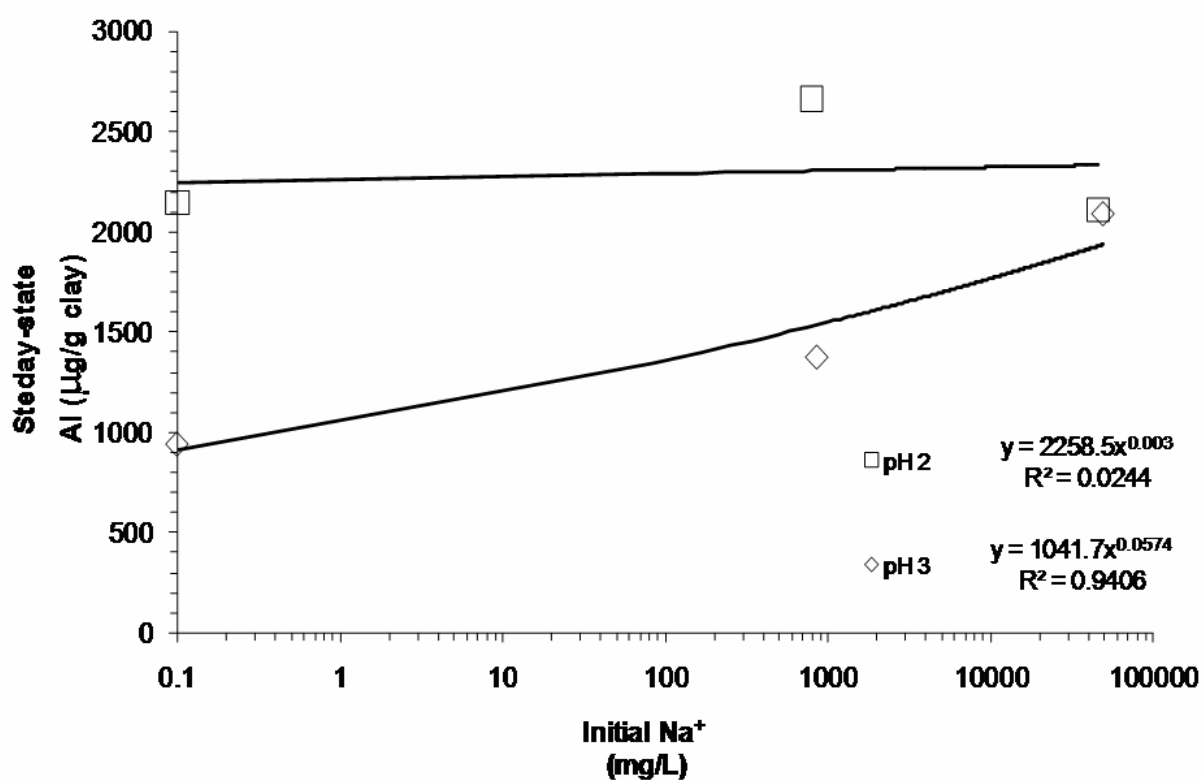


Figure 26. The steady-state levels of Al leached per gram of smectite clay and as a function of the initial sodium levels in the leaching solutions

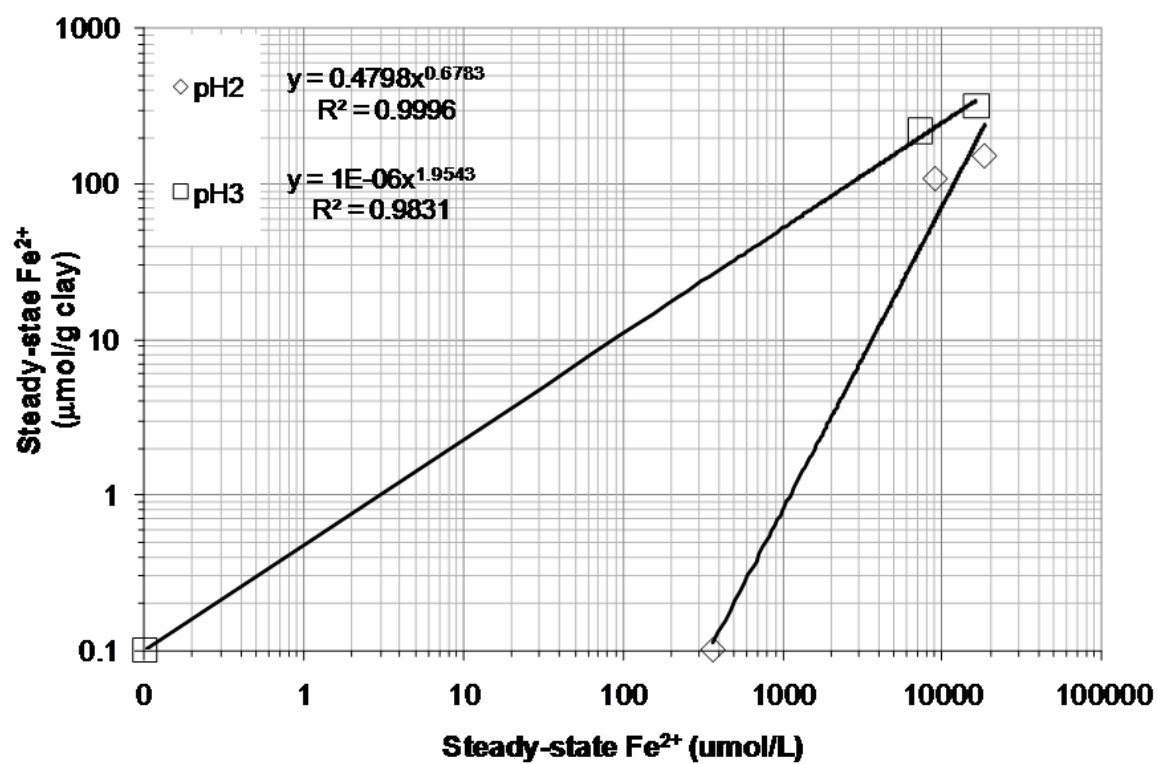


Figure 27. The steady-state levels of Fe^{2+} sorbed per gram of smectite clay and as a function of the steady-state levels of Fe^{2+} in the leaching solutions

4.2.9 Summary from phase 2 leaching

Based on the results from these experiments and as supported by the data in the Appendices A-B, the following conclusions are drawn:

1. The smectite structure is more degraded at pH of 2 than at pH of 3. Thus, low pH values in leaching solutions favor the release of Al and SiO₂ from smectite clays.
2. Extreme K⁺ and Na⁺ levels (~50000 mg/L) in leaching solutions appear to mask the key effect of pH on the release of Al from smectite clays.
3. The higher the initial levels of Fe²⁺, K⁺ and Na⁺ in leaching solutions at pH 2 and 3 the higher the Al and the lower the SiO₂ levels released from smectite clays at steady-state.
4. The release of Al from smectite clay to these leaching solutions containing Fe²⁺, K⁺ and Na⁺ at pH 2 and 3 is caused by ion-exchange and clay dissolution processes.
5. The initial release of Al from smectite clays to these leaching solutions containing Fe²⁺, K⁺ and Na⁺ at pH 2 and 3 is dominated by surface ion-exchange reactions.
6. Overall, the affinity of Fe²⁺ for the smectite surface is higher than the affinity of K⁺ and Na⁺.
7. The release of Si and Al from smectite clays to these leaching solutions containing Fe²⁺, K⁺ and Na⁺ at pH 2 and 3 is dominated by clay dissolution processes in the long-term.

8. The presence of Fe^{2+} , K^+ and Na^+ in leaching solutions at pH 2 and 3 enhances the coagulation of SiO_2 colloidal particles.
9. Thus, the higher the initial Fe^{2+} , K^+ and Na^+ in leaching solutions at pH 2 and 3 the lower the levels of SiO_2 in these leaching solutions at steady-state.
10. The higher the Fe^{2+} , K^+ and Na^+ levels in these leaching solutions the higher the deviation from congruent dissolution of the smectite clay in the long-term.
11. The presence of initial extreme levels of K^+ and Na^+ (~ 50000 mg/L) in leaching solutions at pH 2 and 3 may promote the formation of secondary solid phases containing Al.

5.0 CONCLUSIONS AND SIGNIFICANT RESULTS

In general, the data developed from this PhD research show that the release of aluminum from smectite clays is enhanced by potassium (KCl) and sodium (NaCl) salts leaching solutions at typical pH of 2 and 3 frequently found in field acid mine drainages. Thus, the Al released per gram of smectite clay to brackish AMD/ARD containing Fe^{2+} (~500 mg/L) and Na (~1000 mg/L) and K (~500 mg/L) salts was higher than the Al released to non-brackish AMD/ARD with similar Fe^{2+} (~500 mg/L) at pH 2 and 3. Particularly,

- The Al released per gram of smectite clay to brackish AMD/ARD was 1.2 times higher than the Al released to these non-brackish AMD/ARD at pH 2.
- The Al released per gram of smectite clay to brackish AMD/ARD was 1.4 times higher than the Al released to non-brackish AMD/ARD at pH 3.

The presence of ferrous iron in leaching solutions at these typical pH values of 2 and 3 enhances the release of aluminum from smectite clays as well. Particularly,

- The Al released per gram of smectite clay to non-brackish AMD/ARD containing Fe^{2+} (~500 mg/L) was about 1.9 times higher than the Al released to sulfuric acid solutions at pH 2.

- The Al released per gram of smectite clay to non-brackish AMD/ARD containing Fe^{2+} (~500 mg/L) was about 11.8 times higher than the Al released to sulfuric acid solutions at pH 3.
- The Al released per gram of smectite clay to non-brackish AMD/ARD containing Fe^{2+} (~1000 mg/L) was about 2.4 times higher than the Al released to sulfuric acid solutions at pH 2.
- The Al released per gram of smectite clay to non-brackish AMD/ARD containing Fe^{2+} (~1000 mg/L) was about 21.4 times higher than the Al released to sulfuric acid solutions at pH 3.

Overall, ferrous iron has a higher affinity than potassium and sodium cations for smectite surface sites. Thus, the equivalents as Fe^{2+} sorbed per gram of smectite from non-brackish AMD/ARD containing Fe^{2+} (~500 mg/L) was higher than the equivalents as Na^+ and K^+ sorbed per gram of smectite from brackish AMD/ARD containing Fe^{2+} (~500 mg/L) was higher than the Na^+ (~1000 mg/L) and K^+ (~500 mg/L) at pH 2 and 3. Particularly,

- The equivalents as Fe^{2+} sorbed from non-brackish AMD/ARD was about 215 μeq as $\text{Fe}^{2+}/(\text{g clay})$ as compared to about 52 μeq as $\text{Fe}^{2+}/(\text{g clay})$, 37 μeq as $\text{K}^+/(\text{g clay})$ and 129 μeq as $\text{Na}^+/(\text{g clay})$ sorbed from brackish AMD/ARD at pH 2.
- The equivalents as Fe^{2+} sorbed from non-brackish AMD/ARD was about 439 μeq as $\text{Fe}^{2+}/(\text{g clay})$ as compared to about 298 μeq as $\text{Fe}^{2+}/(\text{g clay})$, 88 μeq as $\text{K}^+/(\text{g clay})$ and 167 μeq as $\text{Na}^+/(\text{g clay})$ sorbed from brackish AMD/ARD at pH 3.

Our experimental results also suggest that extreme concentrations of potassium (around 50000 mg/L) and sodium (around 50000 mg/L) salts in saline AMD/ARD at initial pH values of 2 and 3 lessen the amount of soluble aluminum in solution, apparently due to secondary precipitation reactions. Particularly,

- The Al released per gram of smectite clay to saline AMD/ARD was about 20.7% lower than the Al released to brackish AMD/ARD containing Na (~1000 mg/L) and K (~500 mg/L) salts at pH 2.
- The Al released per gram of smectite clay to saline AMD/ARD was about 34.1% lower than the Al released to brackish AMD/ARD containing Na (~1000 mg/L) and K (~500 mg/L) salts at pH 3.

The exchange and dissolution processes are the major mechanisms of release of aluminum after leaching smectite with synthetic AMD containing different initial high concentrations of ferrous iron, potassium and sodium at pH values of 2 and 3. In general, a first stage of fast release of aluminum from smectite clays suggested that exchange reactions involving ferrous iron, potassium and sodium in leaching solutions and aluminum on the surface of smectite clay took place within the first hours of leaching. This initial rapid release of aluminum was followed by a second stage of slower release of aluminum at a relatively constant rate, in the presence of excess clay, giving the appearance of a zero order reaction. Overall, the ferrous iron, potassium and sodium concentrations in the leaching solutions remained rather stable at pH 2 and 3 or slowly increased at pH 2 during this second stage. This is consistent with slow clay dissolution processes dominating the long-term release of aluminum.

Overall, the analysis of the molar Al/Si ratios in the different leaching solutions support that the initial release of Al from smectite clays to leaching solutions containing Fe^{2+} , K^+ and Na^+ at pH 2 and 3, is dominated by surface exchange reactions. The release of Si and Al from smectite clays to these leaching solutions tends to be driven by clay dissolution processes in the long-term. The higher the Fe^{2+} , K^+ and Na^+ levels in these leaching solutions the higher the deviation from congruent dissolution in the long-term. This is consistent with the formation of secondary solid phases that may contain Al, in leaching solutions containing extreme concentrations of Fe^{2+} (~500 mg/L), K^+ (~50000 mg/L) and Na^+ (~50000 mg/L).

Equilibrium relationships were developed from our experimental data using the steady-state levels of Al leached from smectite clay and the initial Fe^{2+} , K^+ and Na^+ concentrations in leaching solutions at pH of 2 and 3. These equilibrium relationships may assist in the determination of estimates of Al levels leached per gram of smectite clays due to common acid drainages found in field AMD/ARD affected sites.

Acid mine drainage and acid rock drainage are significant environmental issues leading to heightened public sensitivity. Aluminum release into surface waters has resulted in loss of fish life and associated environmental degradation. Aluminum remains one of the least understood AMD/ARD parameters in treatment system design. The Pennsylvania-Bureau of abandoned mine reclamation (PA-BAMR) treatability guidance indicates that AMD with more than 5 mg/L is unsuitable for passive treatment (Cavazza et al., 2008). In order to meet desirable discharge standards for aluminum, there is a need for it to be carefully managed within the treatment system. Thus, one of the most important challenges, regarding the remediation of cases of AMD/ARD, involves the understanding of the physical, and chemical processes governing generation of aluminum-containing AMD/ARD discharges.

When the underground geology, characterized by the presence of clays, such as smectites, is slowly leached with AMD/ARD, the coupled effect of subterranean ion exchange and dissolution processes may release significant amounts of aluminum from field clay soils, resulting in high aluminum concentrations in downslope AMD/ARD seeps. The outcome of this research adds new knowledge to the field of environmental science and engineering by pointing out the significant effects that K and Na salts in AMD/ARD have on the release of aluminum from clays. These K and Na salts in AMD/ARD promote the release of Al from field clays leading to deleterious effects on aquatic ecosystems. Thus, this research contributes to a better understanding of the occurrence of high concentrations of aluminum in AMD/ARD and will assist others to consider alternative remediation strategies in those locations where the in-situ generation of high concentration of aluminum discharges occurs. This work also offers insight into some issues of possible significance. The observation of greater concentrations of aluminum in leachate produced by brackish AMD/ARD implies that highway deicing salts in road runoff could aggravate the leaching of aluminum from pyritic rocks used as fill or exposed in road cuts.

6.0 SUGGESTIONS FOR FUTURE RESEARCH

Through observations and experimental studies it has been shown that underground and brackish acid mine/rock drainage may enhance the release of elevated levels of Al from clays, such as smectites. Thus, preventing the use of K and Na deicing salts should be encouraged, especially in those places where the concomitant occurrence of pyrite and clays has been reported. Soil characterization involving advance instrumental analysis could help to identify those existing pyritic and clay soils. The developed experimental methodology can be applied to these soils to determine the tendency of elevated levels of Al to occur in brackish acid drainages and to contrast the data with that suggested by the design procedure. The use of salt-free deicing agents, such as calcium magnesium acetate, could be a viable alternative to avert leaching of aluminum from these soils. However, further research to assess its leaching potential in AMD/ARD environments should be explored.

If the use of K and Na deicing agents in these areas is preferred or in the presence of brackish (K and Na salts) waters, the use of limestone to increase the pH and prevent the leaching of aluminum from clays may still be viable in these areas. Other alternatives such as the use of grout curtains could also be considered. In such a case, it is also recommended further investigation to assess the suitability of this remediation strategy to prevent brackish acid mine/rock drainages from permeating through clay soils. The efficiency, containment and diverting of brackish and acid drainages should be tested in the long-term through field studies.

These investigations should also address potential issues such as corrosion and incrustation caused by these brackish acid drainages on concrete and metal equipment.

The experimental studies show that the leaching of acid smectite clays initially release significant levels of aluminum due to exchange processes with ferrous iron, potassium and sodium in underground and brackish acid mine/rock drainages. This suggests the potential use of smectite clay composites to capture and recover valuable metals in wastes, such as those generated in metal mining, such as gold. The feasibility and performance efficiency of this technology should be object of study in the future.

APPENDIX A

PHASE 2: LEACHING EXPERIMENTAL DATA AT PH 2

DEIONIZED WATER (D.W.) LEACHING SOLUTION AT PH 5.7										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	0.8	5.7	<1	<2	<2	4.2	<5	13.5	<2	<2
0.5	0.8	3.1	<1	<2	<2	7.4	<5	4.5	<2	<2
22	0.5	3.6	<1	<2	<2	5.3	7	3.7	<2	<2
69	0.6	3.3	<1	<2	<2	4.2	15	4.5	<2	<2
117	0.6	3.3	<1	<2	<2	4.7	16	3.7	<2	<2
243	0.6	3.7	<1	<2	<2	3.2	21	3.7	<2	<2
359	1.8	3.2	<1	<2	<2	2.6	27	2.9	<2	<2
576	0.7	3.7	<1	<2	<2	6.8	31	3.7	<2	<2
693	1.5	3.3	<1	<2	<2	4.2	41	3.7	<2	<2
1053	1.5	3.3	<1	<2	<2	5.3	46	2.9	<2	<2
1246	1.0	3.3	<1	<2	<2	1.7	47	3.7	<2	<2
1413	2.7	3.0	<1	<2	<2	3.3	49	2.9	<2	<2

* Initial composition of stock leaching solution at leaching time t=0 hours. ¹Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

SULFURIC ACID LEACHING SOLUTION AT PH 2										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	0.7	2.1	<1	<2	<2	<2	<5	<2	<2	<2
0.5	0.7	2.1	<1	6	2.5	<2	<5	8.0	4.9	<2
24	0.7	2.1	2.9	7	2.0	<2	16	8.0	6.0	<2
76	2.0	2.2	3.7	8	<2	<2	30	7.3	5.8	<2
167	1.6	2.1	4.8	10	<2	<2	45	6.5	5.8	<2
336	1.8	2.1	5.9	12	3.5	2.8	63	6.5	5.6	<2
508	2.4	2.1	7.3	17	2.5	<2	76	5.8	5.7	<2
647	2.8	2.1	9.0	17	2.5	2.3	86	5.8	5.5	<2
814	2.2	2.0	10.9	21	3.5	3.3	95	5.8	6.0	<2
1037	2.3	2.0	13.1	19	2.5	4.8	114	5.8	5.6	<2
1205	1.5	2.0	13.4	21	2.5	4.3	121	7.3	6.0	<2
1368	2.5	2.0	14.3	21	3.0	5.3	120	6.5	6.4	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD1_500 LEACHING SOLUTION AT PH 2										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	1.5	2.1	<1	583	<2	<2	<5	<2	<2	<2
0.5	1.5	2.1	12.6	444	2.5	<2	<5	10.2	8.3	<2
25	3.0	2.1	16.5	439	<2	<2	17	9.5	8.8	<2
144	2.7	2.1	19.3	465	<2	2.3	40	7.3	8.6	<2
192	1.5	2.1	19.8	474	2.0	<2	46	7.3	8.4	<2
360	2.9	2.1	21.8	477	2.0	2.3	56	6.5	8.0	<2
509	2.6	2.1	22.6	486	3.0	2.3	67	5.8	8.0	<2
673	2.4	2.0	22.6	500	2.5	3.3	68	5.8	7.4	<2
845	3.1	2.0	25.6	503	2.5	2.3	87	4.4	7.7	<2
1039	3.0	2.0	25.4	503	2.0	5.3	95	5.1	7.8	<2
1205	2.8	2.0	28.1	527	3.0	5.3	97	4.4	7.5	<2
1373	2.9	2.0	27.0	494	2.0	5.8	101	5.1	7.7	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD1_1000 LEACHING SOLUTION AT PH 2										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	1.0	2.1	<1	1142	<2	<2	<5	<2	<2	<2
0.5	1.0	2.2	20.9	1024	2	<2	<5	10.9	9.6	<2
20	1.5	2.1	24.8	1001	2	<2	16	9.5	10.2	<2
139	3.0	2.1	27.0	1001	2	<2	31	6.5	8.6	<2
187	3.0	2.1	27.6	1018	<2	<2	42	6.5	8.7	<2
355	2.3	2.1	30.1	1030	<2	2.3	55	6.5	9.5	<2
504	2.7	2.1	30.9	1030	2	<2	81	5.8	9.4	<2
668	2.5	2.0	31.5	1036	<2	<2	67	5.1	8.4	<2
840	2.0	2.0	32.3	1048	<2	2.3	91	4.4	8.6	<2
1034	2.2	2.0	32.6	1030	<2	<2	82	4.4	8.5	<2
1200	2.1	2.0	33.7	1042	<2	<2	87	5.1	8.5	<2
1368	1.6	2.0	33.7	1030	<2	<2	86	5.1	9.5	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD2_500 LEACHING SOLUTION AT PH 2										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	1.1	2.0	<1	583	420	795	<5	2.2	<2	<2
0.5	1.1	2.0	20.6	509	397	748	<5	10.2	9.0	<2
28	2.5	1.9	22.3	509	397	731	17	10.2	9.6	<2
119	2.7	1.9	25.4	515	397	773	39	8.7	9.3	<2
167	1.9	2.0	25.6	527	392	753	36	7.3	8.7	<2
336	2.1	2.0	27.9	541	405	775	51	7.3	8.7	<2
508	3.1	2.0	29.5	547	400	773	70	6.5	8.2	<2
672	2.8	1.9	29.3	550	400	756	62	5.8	7.6	<2
844	3.0	1.9	34.0	571	405	770	83	5.1	8.1	<2
1038	1.8	1.9	34.0	571	395	743	96	5.8	8.0	<2
1205	2.3	2.0	32.0	559	405	753	88	5.1	7.6	<2
1372	2.8	2.1	34.0	565	405	778	94	5.1	7.6	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD2_50000 LEACHING SOLUTION AT PH 2										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	1.8	2.1	<1	480	45291	45805	9.7	24.0	<2	<2
0.5	1.8	2.0	9.3	456	42506	42146	9.7	26.9	8.0	<2
17	1.2	2.0	13.7	465	43772	43610	14.7	23.3	8.1	<2
65	1.5	2.0	17.6	480	44532	46293	22.2	21.1	8.7	<2
162	3.2	2.1	17.6	471	44025	43610	26.3	18.9	8.4	<2
334	2.3	2.1	20.1	483	43772	44341	38.8	18.2	8.9	<2
473	2.6	2.1	25.1	489	44278	45317	32.2	18.2	7.3	<2
640	3.1	2.2	27.9	494	44532	46049	44.7	14.5	7.8	<2
863	1.5	2.1	25.9	506	44025	44585	48.0	15.3	8.4	<2
1031	1.4	2.1	26.5	497	43519	44341	46.3	16.0	8.2	<2
1194	1.9	2.2	25.4	500	43519	45073	51.3	14.5	7.6	<2
1363	1.4	2.1	27.9	494	43772	44341	51.3	14.5	8.2	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

APPENDIX B

PHASE 2: LEACHING EXPERIMENTAL DATA AT PH 3

SULFURIC ACID LEACHING SOLUTION AT PH 3										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	0.8	2.8	<1	<2	<2	<2	<5	3.7	<2	<2
0.5	0.8	2.8	<1	<2	<2	2	<5	3.7	<2	<2
15	1.1	2.8	<1	<2	<2	7	<5	6.1	<2	<2
64	2.4	2.9	<1	<2	<2	5	10	3.7	<2	<2
88	0.9	2.9	<1	<2	<2	3	15	3.7	<2	<2
187	0.9	3.1	<1	<2	<2	3	22	2.9	<2	<2
328	1.8	3.0	<1	<2	<2	5	31	4.5	<2	<2
496	1.5	2.9	<1	<2	<2	5	30	3.7	<2	<2
688	2.7	2.9	<1	<2	<2	4	36	2.9	<2	<2
881	3.0	2.9	<1	<2	<2	<2	41	2.9	<2	<2
1047	2.5	2.9	<1	<2	<2	<2	41	3.7	<2	<2
1215	2.3	2.8	<1	<2	<2	2	45	3.7	<2	<2

* Initial composition of stock leaching solution at leaching time t=0 hours. ¹Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD1_500 LEACHING SOLUTION AT PH 3										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	0.2	3.2	<1	559	<2	2.6	<5	4.5	<2	<2
0.5	0.2	2.6	8.1	402	<2	3.7	<5	10.2	6.7	<2
27	2.5	2.6	10.3	427	<2	4.7	7	7.8	7.5	<2
71	0.8	2.7	10.7	420	<2	4.7	13	6.1	7.2	<2
170	1.3	2.8	11.2	416	<2	4.7	20	6.1	7.2	<2
239	1.0	2.7	10.7	405	<2	6.3	25	6.1	7.2	<2
406	1.8	2.7	10.7	405	<2	6.3	28	5.3	6.4	<2
579	2.0	2.7	10.7	409	<2	4.7	34	5.3	6.9	<2
743	2.6	2.7	11.7	413	<2	5.3	41	4.5	7.0	<2
916	2.4	2.6	11.9	409	<2	4.9	39	5.3	6.7	<2
1083	2.5	2.6	11.9	395	<2	4.9	41	5.3	6.7	<2
1251	2.7	2.5	11.7	405	<2	4.9	43	5.3	6.6	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD1_1000 LEACHING SOLUTION AT PH 3										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	0.8	3.1	<1	1132	<2	<2	<5	2.9	<2	<2
0.5	0.8	2.6	16.0	939	<2	<2	<5	8.6	7.8	<2
23	0.4	2.7	17.9	939	<2	<2	7	6.9	7.6	<2
67	0.8	2.7	18.6	925	<2	<2	12	6.1	7.2	<2
166	1.4	2.8	19.5	925	<2	<2	22	5.3	7.2	<2
235	1.0	2.8	19.3	918	<2	<2	25	5.3	7.0	<2
402	2.5	2.8	19.5	918	<2	<2	28	4.5	6.7	<2
575	3.0	2.8	21.2	904	<2	<2	33	5.3	7.3	<2
739	1.5	2.6	21.2	918	<2	<2	38	4.5	6.9	<2
912	2.5	2.6	21.5	904	<2	<2	41	4.5	7.2	<2
1079	2.7	2.6	21.5	918	<2	<2	38	4.5	6.9	<2
1248	3.0	2.5	21.7	911	<2	<2	40	4.5	6.9	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD2_500 LEACHING SOLUTION AT PH 3										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	0.1	3.2	<1	548	448	851	<5	2.9	<2	<2
0.5	0.1	2.7	11.5	416	376	783	<5	7.8	6.9	<2
23	0.5	2.7	14.5	427	393	804	6	7.8	7.6	<2
47	1.5	2.8	14.5	416	384	772	10	6.1	7.0	<2
146	1.0	2.9	14.8	438	398	799	16	6.9	7.3	<2
239	1.6	2.7	15.0	441	412	801	21	6.1	7.5	<2
406	2.0	2.8	16.9	445	401	799	27	7.8	7.6	<2
579	3.0	2.9	17.6	452	409	801	33	4.5	7.3	<2
743	1.5	2.8	16.7	441	398	799	33	5.3	6.7	<2
916	2.3	2.8	17.4	441	407	806	39	5.3	6.6	<2
1083	2.5	2.7	16.9	448	407	803	38	4.5	6.6	<2
1251	2.9	2.7	17.2	438	404	806	41	4.5	6.6	<2

* **Initial composition of stock leaching solution at leaching time t=0 hours.** ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

AMD2_50000 LEACHING SOLUTION AT PH 3										
Time (hr)	DO (mg/L)	pH	^{1,2} Al (mg/L)	¹ Fe (mg/L)	¹ K (mg/L)	¹ Na (mg/L)	^{1,2} SiO ₂ (mg/L)	¹ Ca (mg/L)	¹ Mg (mg/L)	¹ Mn (mg/L)
*0	0.2	3.1	<1	434	45111	48258	7	20.8	<2	2.0
0.5	0.2	2.6	22.4	427	42611	46653	9	19.2	6.0	2.6
47	1.0	2.7	29.1	413	40944	46390	16	15.9	5.8	2.0
91	1.5	2.8	23.1	413	43167	46390	16	16.7	6.4	2.3
188	0.9	2.8	26.0	434	44833	48232	26	15.1	6.4	2.3
356	0.7	2.9	24.3	430	43722	48232	32	13.5	6.3	2.3
548	2.3	2.8	26.5	420	43722	46390	37	12.7	6.3	2.3
741	2.9	2.8	26.5	434	43444	49021	36	11.8	6.4	2.3
907	3.0	2.8	25.5	430	44556	48495	38	12.7	6.1	2.3
1075	2.5	2.8	26.2	427	44000	48763	39	11.8	6.0	2.0
1244	1.7	2.9	25.7	427	43444	48763	42	12.7	6.4	2.0

* Initial composition of stock leaching solution at leaching time t=0 hours. ¹ Practical quantitation limits (PQL) were: 1 mg/L for Al; 2 mg/L for Fe, K, Na, Ca,, Mg and Mn; and 5 mg/L for SiO₂. ²Determination of Al and SiO₂ with non-digested samples

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